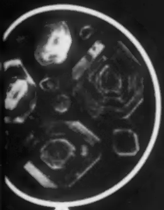
CHEMISTRY



FEBRUARY
1960

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Editorial:
New Approaches
Inside Front Cover

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A SCIENCE SERVICE PUBLICATION

New Approaches

➤ IT IS A COMMON COMPLAINT of college students majoring in chemistry that most of their freshman year is "wasted" in repeating high school chemistry. Their teachers, on the other hand, complain that first year chemistry majors are often sadly lacking in the basic fundamentals of their subject.

This problem is by no means limited to the field of chemistry; the same complaints may be heard in any scientific department of a university. What is being done about it?

The National Science Foundation is particularly concerned, and has granted funds to many groups of scientific educators who are working on new courses in several fields and at most levels. The following is an extract from an N. S. F. report on these projects:

"A series of grants is enabling a group of college and university chemists and high school teachers, organized as the Chemical Bond Approach Committee, to devise a high school course using the concept of chemical bonding as the central theme. The preliminary version of the textbook, laboratory guide, and teacher's guide is being tested in several schools during the current academic year.

"Through a grant to the Ohio State University another group of chemists is planning the organization of a major effort to develop improved high school chemistdy courses along somewhat different lines.

"At the Johns Hopkins University a new freshman chemistry program is being developed which includes design of apparatus for relatively sophisticated experiments, and films of dynamic lecture demonstrations.

"Support was granted to State University of Iowa for making a film showing how to prepare new types of models of molecules and crystals and how to use them in teaching."

We intend, over the next few months, to bring you descriptions of as many of these and other independent projects as we can. Our lead today is the first such report.

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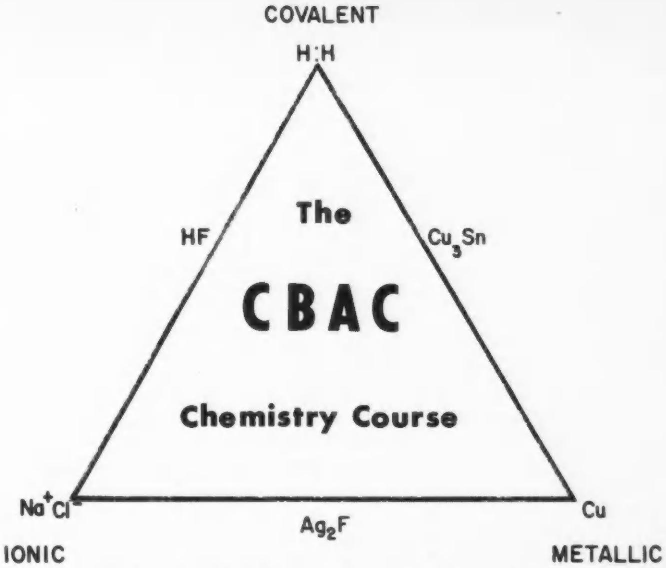

A NEW introductory chemistry course is on trial in several high schools and colleges across the country. This approach to chemistry originated at a conference held in June, 1957 at Reed College, Portland, Oregon.[1] Out of this meeting held to discuss the relationship between high school and college chemistry came the suggestion that any beginning course should have a clearly recognizable central theme and that "chemical bonds" was the logical central theme. This choice of theme was motivated by the observation that it is the chemical bond which distinguishes chemistry from related disciplines. The making and breaking of these links between atoms *is* chemistry. Several teachers used the proposed course outline[2] the following academic year. A year later some members of the Wesleyan Conference[3] again considered the chemical bond approach fruitful and recommended that it be tried in a larger group of high schools on an experimental basis. Continued support from the National Science Foundation permitted a six-week writing conference to be held at Reed College during the summer of 1959.[4] The seventeen full-time participants and eleven visitors produced about 1000 pages of rough draft material. At the same time a further grant was received from the National Science Foundation for continued production of textual

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[1] J. Chem. Ed. 35, 54 (1958).

[2] L. E. Strong and M. K. Wilson, J. Chem. Ed. 35, 56 (1958).

[3] M. G. Burford and H. F. Lewis, J. Chem. Ed. 36, 90 (1959).

[4] A. H. Livermore and L. E. Strong, J. Chem. Ed. (in press).

material and trial of the program in nine high schools. The project is now centered at Earlham College and is under the direction of L. E. Strong (Earlham College), L. B. Clapp (Brown University), A. H. Livermore (Reed College), H. A. Neidig (Lebanon Valley College), and M. K. Wilson (Tufts University). At present two volumes of textual material comprising nine chapters, the laboratory manual for the first semester, and the teacher's laboratory guide for the first semester have been published by photographic offset from typed copy. Material for the second semester laboratory course is at the printer as are the next four chapters of the text. The final four chapters are in preliminary draft.

In the main the suggestions contained in the original outline[2] have been incorporated into the course. It is assumed that today any student accepts the existence of atoms and electrons and is willing to consider their use in explaining macroscopic properties of substances. Therefore, no attempt is made to give a systematic proof for the existence of these entities. Throughout the course attention is focused upon the physical and chemical properties the various types of chemical bonds impart to substances and, conversely, the possibility of inferring the bonding present in molecules from the observation of physical and chemical properties. Chemists deal with aggregates of atoms and the properties of these aggregates are largely determined by the forces between atoms. These forces are responsible for the aggregation. For the purposes of this course, chemical bonds are divided into three categories: covalent, ionic, and metallic. Polar covalent bonds are discussed to indicate the possibilities intermediate between covalent and ionic bonds and to emphasize that the three classifications are not free from overlap.

The bonding theme requires the introduction of considerable material related to atomic structure which most properly should occur in a physics course. Since no such prerequisite can be assumed, however, atomic orbitals and energy levels are discussed early and lead into an extensive discussion of molecular orbitals and molecular geometry.

Thus, Chapter IV entitled "Electrons in Orbitals" discusses the masses of atoms, the charge and mass of the proton, neutron, and electron, and the electron configuration of atoms up to calcium. Energy levels are based upon ionization energies rather than on spectroscopic evidence.

Chapter VI is concerned with covalently bonded molecules. The following constitutes the first five sections of Chapter VI:

Chemical Change: Covalent Chemical Bonds

Chemical Change

"You have already been shown some of the manifestations of changes that can occur by physical means. Powdered sugar and granulated sugar have different properties (ask a cook!) although one is made from the other by a simple physical change (crushing). When a glass tumbler is broken, we know the pieces are still glass and have many of the properties of the original glass but a physical change has occurred and at least one property is lost: the tumbler will no longer hold water. Ice, water, and steam are manifestations of the same substance, H_2O, in three different states. Syrup is a water solution of the white crystalline substance we call sugar. The appearance is quite different but syrup and sugar can serve the same purpose in many places — to sweeten.

"Now we are ready to study changes that a chemist considers to be of a more profound nature than those just mentioned. You know that coal burns, mufflers rust, cider ferments, paint fades, wood decays and that a battery will help to start a car. If you were on the inside of any of these things what would you see? Unfortunately we can't answer all these questions in this course but we hope to arouse your curiosity so that you will want to read further to find the answers.

"The chemist suggests that coal, charcoal, coke, graphite, and the diamond are essentially the same element carbon. How can you possibly believe that this is so? Coal is a soft, black, dirty material, while a diamond, besides being a girl's best friend, is one of the hardest substances known, will scratch metals, has a density of 3.5 g/ml and is a non-conductor of electricity. Graphite, the other pure form of carbon has a density of 2.2 g/ml, is easily crushed and has a slick feel. How can the same element exhibit such divergent properties? The other substances, coal, charcoal, and coke are microcrystalline forms, but not pure carbon.

"It is easy enough to show that diamond and graphite both consist of the element carbon. Lavoisier (about 1790) burned a diamond in oxygen and found that the only product was carbon dioxide. Graphite also burns to give the same product. These are chemical changes.

by symbols:	C	$+$	O_2	$\rightarrow$	CO_2
by weight:	12		32		44
by name:	diamond or graphite		oxygen		carbon dioxide

When done on a quantitative basis, as we have learned, the production of 44 parts by weight of CO_2 for each 12 parts of carbon would be proof that all of the starting substance was carbon, once we accept the meaning of the symbols and the equation used.

"If we accept this experimental evidence, then the difference between graphite and diamond must be sought in the internal make-up, i.e., structure. We will pursue this idea further but let's ask some more questions first.

"From Table 1 it is to be noted that diamond or graphite (both carbon) with the widely differing properties already mentioned and hydrogen, a colorless gas with very low boiling point are somehow combined in methane, CH_4, a colorless gas of still different properties. How can such a profound change occur?

"If we examine another series of compounds, CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, where the apparent change is a replacement of H by Cl successively, the starting compound, a gas, goes through a succession of changes in which the boiling point rises from —161° to 76° in CCl_4. This is a more orderly change than the abrupt change in the properties

TABLE 1

Properties of Various Substances

		B.P. °C	M.P. °C	Density			Electrical Conductor		Clarity	Color
				Solid	Liquid	Gas (STP)	Solid	Liquid		
Ne		−245.9	−248.7		1.204	0.674 (A)	No	No	Clear	Colorless
Ar		−185.7	−189.2		1.402	1.38 (A)	No	No	Clear	Colorless
H_2		−252.7	−259.1		0.0709	.06948 (A)	No	No	Clear	Colorless
CH_4		−161.4	−184			.554	No	No	Clear	Colorless
CCl_4		76.8	− 22.6		1.595		No	No	Clear	Colorless
C	graphite			2.25			Yes		Opaque	Black
	diamond	3470 (subl.)		3.51			No		Clear	Colorless
SiO_2 (quartz)		2230	1425	2.65			No	No	Clear	Colorless
Cu		2310	1083.	8.92			Yes	Yes	Opaque	Yel - red
Na		880	97.5	0.97			Yes	Yes	Opaque	Silver
Fe		3000	1535.	7.86			Yes	Yes	Opaque	Silver
$MgZn_2$			595				Yes	Yes	Opaque	Silver
CuZn (brass)			470				Yes	Yes	Opaque	Yellow
Na^+Cl^-		1413	804	2.163			No	Yes	Clear	Colorless
K^+F^-		1500	880	2.48			No	Yes	Clear	Colorless
$Mg^{++}(Br^-)_2$			700	3.72			No	Yes	Clear	Colorless

of diamond, hydrogen, and methane.

"How can we make any sense out of this puzzle? Is there any attribute of these various substances that will throw light on all the questions raised? One important aspect of the changes involved is structure. Before the questions can be answered, we must first turn to a closer look at atomic and molecular structure.

Classification of Substances

"How are we to choose examples from among the millions of different materials known? Indeed, why did we pick the substances in Table 1 to discuss in here? If an arbitrary or miscellaneous collection of materials is discussed, then what is concluded about these can hardly have much application to all the others. Clearly the problem of choosing examples can be resolved only by some kind of preliminary classification procedure.

"Upon what basis, then, can we divide the great variety of materials known into groups? It is possible to separate all materials into one or more pure substances. There are straightforward laboratory procedures for carrying out the necessary steps. It is possible to go one step further and subdivide all pure substances into two groups, of which one is a small number of substances called chemical elements.

"Unfortunately, the remaining pure substances, which are compounds of two or more different elements, number something over a million. Among all these compounds are ones exhibiting a great variety of properties. A few examples are presented in Table 1 to illustrate the range of behavior. How can we organize compounds in a way that will make possible a meaningful discussion? It is clearly impractical to discuss each substance by itself.

"A further basis for subdivision has been mentioned based on bond type. Chemists deal with fairly large amounts of material ordinarily. In these pieces of material forces operate to hold the material together. These forces are referred to as bonds. The bonds are the glue which hold atoms together in some appropriate structure. The great variety of substances known do not seem to be easily understood as the result of a single type of bond but rather of several.

"If we consider the properties listed for substances in Table 1, at least three different sets are discernible. Hydrogen, methane, and carbon tetrachloride form one set with properties rather similar to those of neon and argon. In this set boiling and melting points are at rather low temperatures, but even more noticeable is the short temperature interval within which each of these substances is a liquid. These substances are transparent, colorless, and non-conductors of electricity. It is this type of substance which exemplifies the covalent bond.

"A second set of substances with properties markedly different from the first is illustrated in Table 1 by copper, sodium, iron and two alloys. In this set boiling points are of the order of 1,000° C, and the materials exist as liquid over an extended range of temperature. Uniformly such substances are opaque, and most of them are silvery colored. This type of substance exhibits the metallic bond.

"Sodium chloride, potassium, fluoride, and magnesium bromide are representatives of still a third type. In this type, boiling points are high, and the material can be liquid over a temperature interval of the order of 500° C. They differ from the metals in being transparent and usually colorless. As solids they are non-conductors of electricity, whereas metals are conductors. This third group of materials exemplifies the ionic bond type.

"The triangular diagram on page 1 depicts this three-fold division of all compounds. Unfortunately, substances are not found in nature neatly labeled as to which type they belong until a chemist chooses to do so. More than a few compounds do not fit simply into the man-made classification presented here. Two such examples are included in Table 1, carbon and quartz. Their properties can be accounted for, and will be discussed in some detail later in this chapter. Subsequent chapters will take up other kinds of substances which do not fit the simple three-part classification.

"Let us now enter into a more detailed study of each of these bond types. This study has as its purpose the understanding of how substances enter into reactions, and how reaction products are related to initial reagents. In this chapter we will consider the first or covalently bonded substances. To do this it is necessary to explore the nature of electron arrangements within atoms and molecules.

Atomic Orbitals

"In the discussion of the nature of the electron, two reconcilable views were given. An electron may sometimes advantageously be considered a particle and at other times a wave. As a wave we may consider an electron to be a cloud of negative electricity. It is only fair to ask then, 'What shape and character does the cloud have?' Is it a black, dense, storm cloud or a fleecy, light, cumulus cloud? The cloud of negative electricity has been described variously depending on its level of energy. Intuition might lead one to suggest that the electron should surround the nucleus of the atom in a spherical shape. Intuition leads to a satisfactory description for the *s* electron. The portion of space reserved for occupation by an electron cloud is called an orbital. Just as a cloud in the sky has a shape determined by the way the winds blow on it, so a cloud of negative electricity has a shape determined by the action of electrical forces.

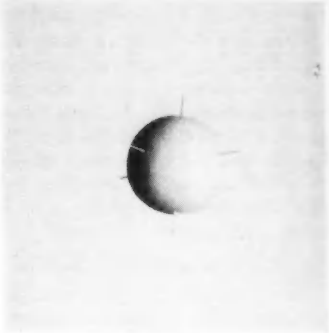

Fig. 1

Perspective representation of the atomic 1s orbital.

"It should be mentioned that the 2s orbital also exists for the hydrogen atom but the energy level of the 2s orbital is so much above the 1s orbital that the 1s orbital is occupied first under ordinary conditions. The reservation is there, however, whether the Indian is in residence or not.

"The way in which the electronic

configurations of the first elements in the periodic table are built up was shown in Chapter IV. The *s* orbitals (Fig. 1) consist of concentric spheres of increasing radius (1s, 2s, 3s, etc.) while *p* orbitals (Fig. 2) are dumbbell in shape (2p, 3p, etc.) at right angles to each other. In an atom such as silicon, the electronic configuration will give a cluttered picture if all the orbitals are shown at once — three concentric spheres of increasing radius (1s, 2s, 3s) together with five *p* orbitals, (three in 2p level and two in 3p level) each of which is a dumbbell shape.

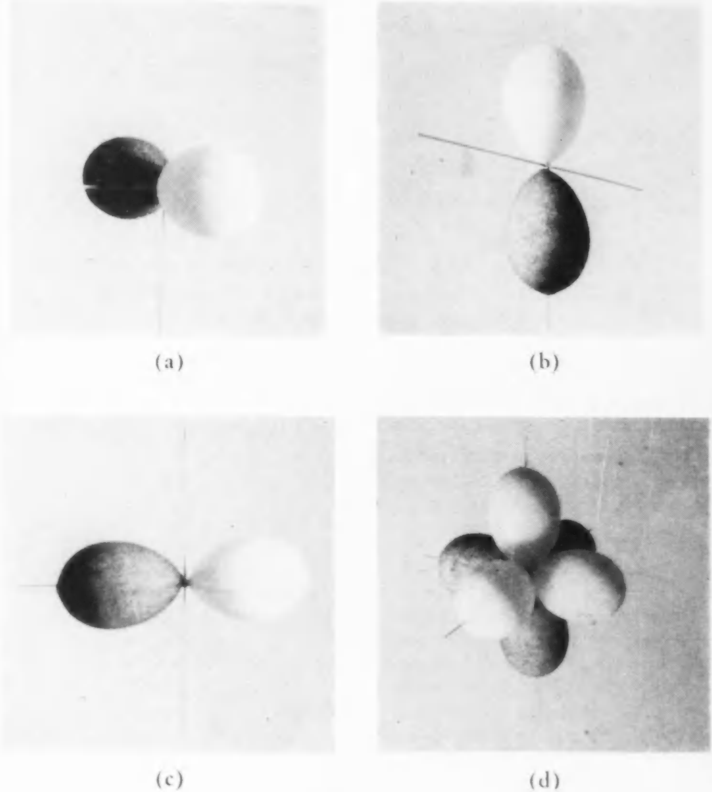

Fig. 2

Perspective representation of p_x, p_y, p_z atomic orbitals (a, b, c) superimposed in (d) to show orientation in x, y, z planes.

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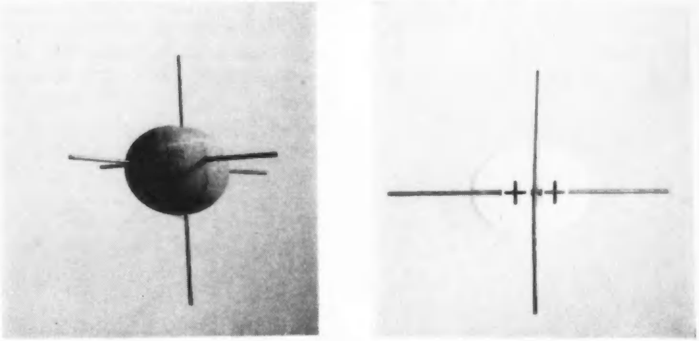
Molecule Formation

"Molecule formation from two atoms by this model involves the interpenetration of atomic orbitals to the point at which mutual repulsion of nucleus for nucleus and electron cloud for electron cloud balances mutual attraction of positive nuclei for negative electron cloud in the two atoms. The covalent bond so formed *is* the pair of electrons. Bond formation cannot occur unless the electrons involved have opposite spins. Covalent bonds are characterized then by the sharing of



(a) (b)

Fig. 3

Representation of hydrogen molecule (a) in perspective and (b) in cross section through the nuclei.

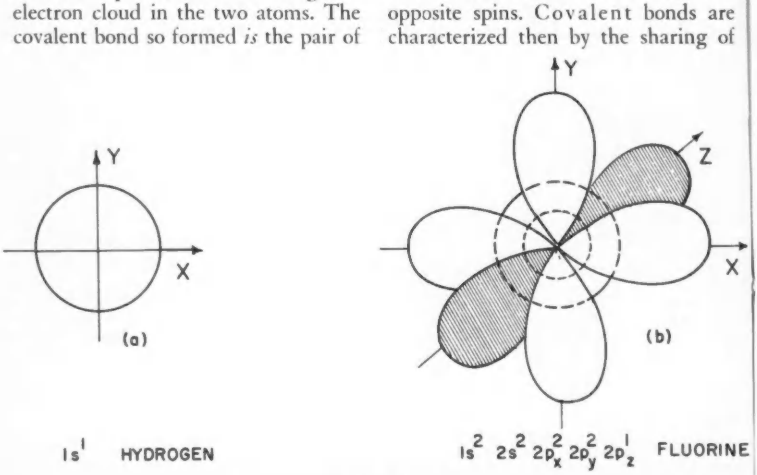


Fig. 4

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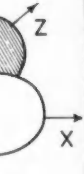

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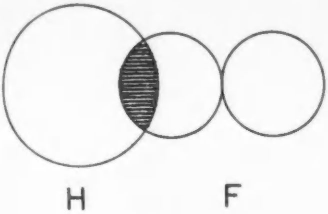


Fig. 5
Combination of the hydrogen 1s orbital with the fluorine 2p orbital.

a pair of electrons. The interpenetration of two spherical *s* orbitals from two hydrogen atoms results in a molecule whose electron cover is egg-shaped. The shared pair is now said to belong to the orbital of both atoms. The bond between hydrogen atoms may then be called an *s-s* bond, and by abbreviated notation we would write H-H to represent the hydrogen molecule. If a hydrogen and fluorine atom get together the *s* electron in hydrogen is available for bond formation but the *s* electrons in both 1s and 2s orbitals of fluorine are paired and already full. Two *p* orbitals are also not available for bond formation. The third *p* orbital, however, containing one unpaired electron may at a suitable distance overlap the spherical *s* orbital of hydrogen to form a bond between the two. It may be described as an *s-p* bond and the compound may be written H-F.

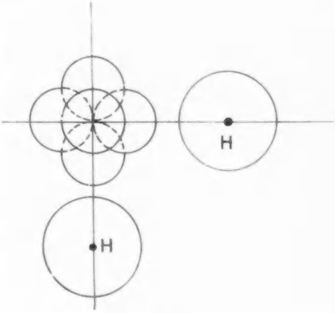


Fig. 6
Atomic orbitals of hydrogen and oxygen. The third *p* orbital of oxygen containing a pair of electrons and perpendicular to the plane of the paper is represented by the inner circle.

"Now let us consider molecule formation between hydrogen and oxygen. Oxygen has two available *p* orbitals for bond formation with an *s* orbital of hydrogen. The formula for water then must reflect this since two hydrogens must be used to supply enough electrons to fill the two *p* orbitals of oxygen. We write it H_2O and the bonds may be described as two *s-p* bonds. If our theory of bond formation is adequate, the bonds from H to O should form an angle of 90° and the molecule of water could be said to have a V-shape. Measurement of the angle at oxygen by X-ray diffraction methods reveals the angle to be 104°27′. This is too far away from

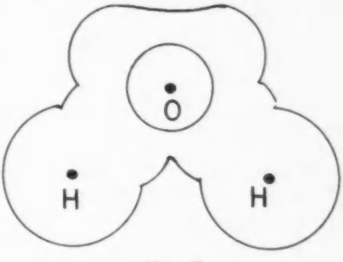


Fig. 7
Representation of water molecule. Overlapping of atomic orbitals to give two *s-p* bonds.

the theoretical value to leave a comfortable feeling about the picture we have given. However, one factor has not been considered. The two hydrogen nuclei are positively charged and conceivably could repel each other enough to increase the angle above 90°. One check of this idea comes through considering the element next below oxygen in the periodic table. Sulfur should form a compound analogous to water with the formula H_2S since the electronic structures of the outermost orbitals are similar. The larger sulfur atom results in a bond longer for SH than for OH. Hence the two hydrogens are held farther apart and repulsion between them should be smaller. We would then

O $1s^22s^22p_x^22p_y^12p_z^1$
S $1s^22s^22p^63s^23p_x^23p_y^13p_z^1$

expect the angle at sulfur to be nearer the theoretical 90°. It is in fact 92°20′ and leaves the theory in a satisfactory position.

"Similar consideration of molecule formation between nitrogen and hydrogen leads to the formula NH_3 and angles of 90° for the H-N-H bonds. Measurement of the angle gives a value 106°45′, again in a wide deviation from theory. However, analogous compounds from other elements in Group V give angles nearer the theoretical value of 90° in accordance with the argument just given for H_2S and H_2O.

TABLE 2
Bond Angles

NH_3	- 106°45′	AsH_3	- 91°35′
PH_3	- 93°50′	SbH_3	- 91°30′

Hybridization

"The electrons in carbon have already been described by the notation $1s^22s^22p_x^12p_y^1$. Two unpaired electrons suggest that carbon should form two bonds with other atoms. One of the major facts of chemistry, however, is the abundance of known carbon compounds in which four bonds, not two, hold the molecule together. To account for this it must be assumed that the arrangement of electrons given above is changed. If one of the $2s^2$ electrons were promoted to the $2p_z$

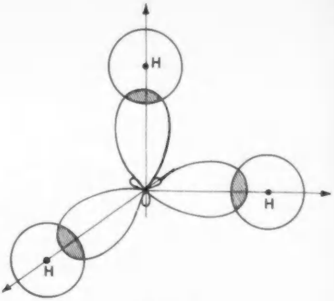


Fig. 8
Representation of ammonia molecule. Overlapping of atomic orbitals to give three *s-p* bonds.

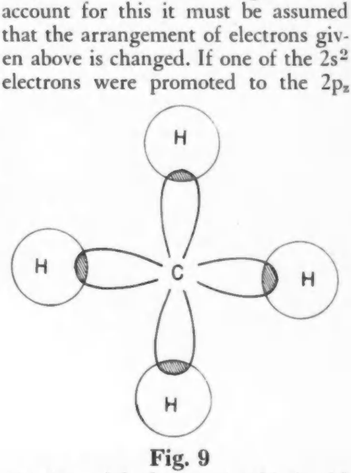
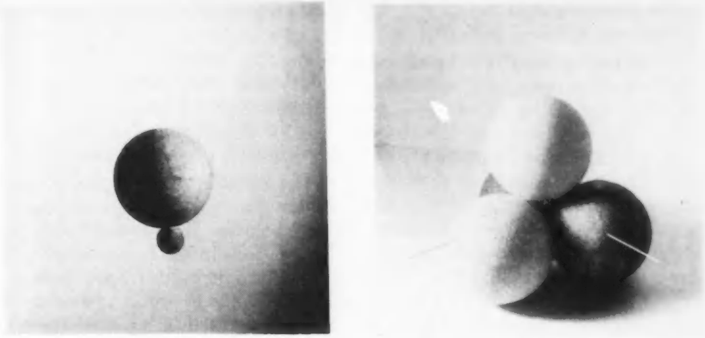


Fig. 9
Overlap of hydrogen *s* orbital with four sp^3 hybrid orbitals of carbon.



(a) (b)

Fig. 10

(a) A single sp^3 hybrid atomic orbital.

(b) Perspective of four sp^3 hybrid orbitals.

orbital, four half-filled orbitals become available for bond formation. This would provide for one *s* and three *p* bonds, the latter at right angles to each other and the *s* bond non-directional. Such is not the case. Instead, a different type of bond is formed, in general, stronger than an *s-s*, *s-p*, or *p-p* bond. Since it comes from crossbreeding of an *s* and three *p* orbitals, it is referred to as an sp^3 hybrid bond. The four bonds thus available are directed to the corners of a regular tetrahedron. If only one node is shown the orbitals would be well represented by Fig. 9. If carbon were to form a compound with hydrogen four s-sp^3 bonds would obtain in CH_4 and with chlorine four p-sp^3 bonds in CCl_4. The three dimensional structure is a

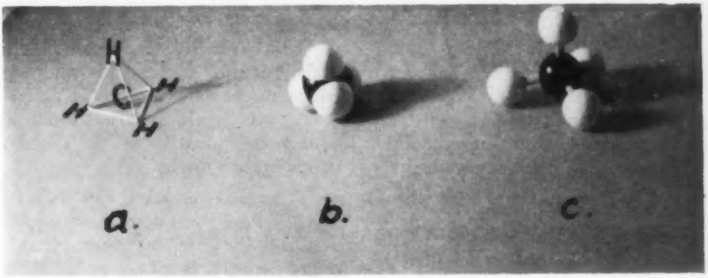


Fig. 11

Three representations of methane: (a) Tetrahedral, shows bonds of carbon atom directed to corners of a regular tetrahedron. (b) Stuart models using correct interatomic distance on the scale 1.5 cm = 1 Å. (c) Ball and stick model which shows only angles and order in which atoms are linked.

regular tetrahedron in which the angles between bonds is 109°28′.

"[It is not expected that you will accept the shape of an sp^3 hybrid orbital (Fig. 10a) as logical or even reasonable. We suggested that the shape of an *s* orbital was reasonable by simple intuition. Not so with the dumbbell shape of the *p* orbital. But we did find it useful in accounting for the shape of water, ammonia and other suggested molecules. The shape of the *p* orbital arises from a solution of the wave equation that describes the behavior of *p* electrons. We ask you to accept this solution of the wave equation as a working hypothesis — that a *p* orbital has a dumbbell shape and a sp^3 hybrid orbital the shape shown in Fig. 10a.

"It is well to note that the shape of the hybrid orbital is quite different from the dumbbell. In the model, this suggests a reason why the dumbbell cannot overlap on both ends. As soon as the overlap on one end occurs the orbital no longer has the dumbbell shape but is now an sp^3 orbital. Without using the model we would arrive at the same conclusion by saying that an orbital cannot be occupied by four electrons at the same time (Pauli exclusion principle) but only two.

"We do not hide the fact that there must be a leap in your thinking about these models but it is because we have asked the model a very difficult question, "What new shape do you get if you mix or add one balloon (*s* orbital) and three dumbbells (*p* orbitals)"? One cannot expect an answer from the models; hence, a leap in our thinking is required.

"Part of the difficulty arises because we are using geometric models for mathematical expressions that were not necessarily meant to have geometric implications. But scientists like models and find them useful. In fact, you will be using analogies and models throughout your scientific career whenever they appear worthwhile.

"If you will make this leap in your thinking, we promise smoother sailing after the leap. Rest assured that you are not alone in the boat. Indeed most of the authors of this book have not gone through the rigorous mathematical analysis that is required to solve the wave equation. We have accepted this solution and the model on a working basis.

"We hope that you will pursue science and mathematics far enough so that some day you can handle the equations involved in the wave mechanics. In the meantime you will find the styrofoam models of orbitals and atoms in your laboratory very helpful in seeing three-dimensional pictures that of necessity appear in perspective on paper.]

"Hybridization is not a phenomenon peculiar to carbon or to other atoms in group IV. The two elements preceding carbon in the periodic table, beryllium and boron and other elements in the same groups II and III also form hybrid bonds. Indeed, in total number, most of the covalent bonds known are hybrid bonds.

"The electronic structure of beryllium, $1s^2 2s^2$ would at first suggest that this element was inert (two *s* orbitals filled). It cannot be called inert, however, and does form two covalent bonds with chlorine, for example. Again it is suggested that promotion of a 2s electron to a 2p level and hybridization of the two orbitals when they are filled by electrons from other atoms will account for the existence of such a compound as $BeCl_2$. The bonding electrons from the two hydrogens are *s* electrons. From beryllium, *sp* hybrid bonds lead to the description *s-sp* for the two bonds in $BeCl_2$.

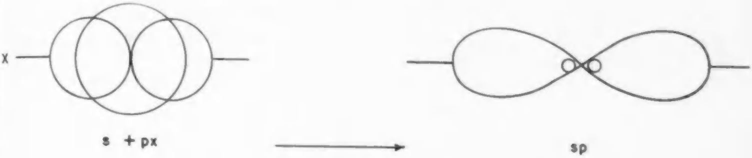


Fig. 12

Formation of *sp* hybrid orbitals from *s* and *p* orbitals.

"In boron, number 5 in the periodic table, the electronic configuration $1s^2 2s^2 2p^1$ again might suggest that boron could form only one covalent bond with other atoms. Such is not the case. Three covalent bonds are formed which we can account for if one 2s electron is promoted to a 2p level. Hybridization of the three bonds from one *s* and two *p* electrons ($2s^1 2p_x^1 2p_y^1$) results in sp^2 hybrid bonding in molecules like BF_3 and BCl_3.

Since *p* electrons are involved from chlorine or fluorine the three bonds are described as p-sp^2 bonds.

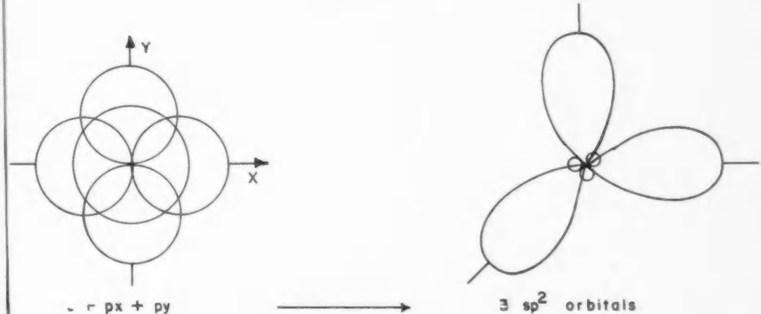


Fig. 13

Hybridization of *s* and two *p* orbitals to 3 sp^2 orbitals.

"The resulting equivalent *sp* hybrid bonds are linear and sp^2 hybrid bonds are planar, making angles of 120° with one another. (Fig. 13)

"Hybridization of orbitals bears some resemblance to a case in nature with which you are familiar. The cross-breeding of a horse and a jackass results in a mule, a wonderful animal with properties of neither parent: toughness, lackadaisical attitude, ability to stand hot weather. A hybrid *sp* bond is stronger than either the *s* or *p* bond and the directional character is different: an *s* electron is non-directional; *p* electrons are dumbbell in shape mutually at right angles to each other; *sp* hybrid orbitals are linear (180°); sp^2 hybrid orbitals are planar at 120°; and sp^3 hybrid orbitals are tetrahedral at 109°28′. All are stronger than their unhybridized counterparts."

Chapter VII treats some energy changes and rates of chemical reactions. Here the concept of "free energy" is introduced and illustrated by simple physical and chemical examples. The chain reaction mechanisms of the H_2-Cl_2 reaction is discussed.

Chapter VIII considers the periodicity of atomic properties such as ionization potential, size, etc. The discussion of atomic size in terms of various radii is as follows:

Meaning of the Size of an Atom

"The 'screening effect' of the inner shells of electrons in decreasing the first ionization potentials of the elements is added to another effect of the inner shells, namely, that the size of the atom increases as the number of inner shells increases. Hence the outer electrons are pushed farther and farther away from the nucleus and the attractive force becomes smaller and smaller.

"How do the sizes of atoms change with their position in the periodic table?

"A qualitative answer to this question seems easy. We would expect the size to depend upon the nuclear charge, since a high nuclear charge would tend to pull the electrons in close to the nucleus. Hence atoms of higher atomic number should be smaller than atoms of lower atomic number.

"The answer does not seem so easy, however, when we remember that the attraction of the nucleus is modified by the screening effect of the inner electron shells and their tendency to keep the outer electrons from approaching the nucleus. If these effects are important enough, they might even make our first answer incorrect, so that atoms of higher nuclear charge were actually bigger than atoms of lower nuclear charge. In an experimental science, we do not settle such questions by argument but by going to the laboratory. The solution seems to be to measure the atom, to determine its radius or diameter, and find out which of these opposing effects is more important. We have said, however, that atoms are nuclei surrounded by fuzzy electron clouds. How does one find where the cloud ends?

"If we consider the question, we will realize that we are not nearly so much interested in finding out where the electron cloud ends for an isolated atom, as we are in finding out how close another atom with its electron cloud can approach it. Such approach may or may not lead to binding, and as chemists, we want to know how close atoms may approach without combining to form a compound, and how close they are when they have formed compounds. This distance *between* atoms is a quantity we can measure, because this is effectively the distance between the centers of the electron clouds, that is, the distance between the nuclei. If we imagine spherical atoms in contact along the line joining the two nuclei, then we may assign a portion of this distance to one nucleus and the remainder to the other. These two distances will then be the radii of the two atoms, assumed to be spheres (Fig. 14). There are several difficulties here. In the first place, the distance *a* will depend upon whether the atoms are bound together in a compound or not bound together. Secondly, there is no certainty that a given atom will keep the same radius when bound to one kind of atom that it had when bound to another kind of atom, so that it may not be sensible even to try to assign a particular value to the radius of a combined atom. There may be as many radii for the atom as there are compounds containing that atom. Thirdly, even if the atom keeps a fairly definite value for its radius in most compounds, how shall we divide the measured distance *a* between the two atoms?

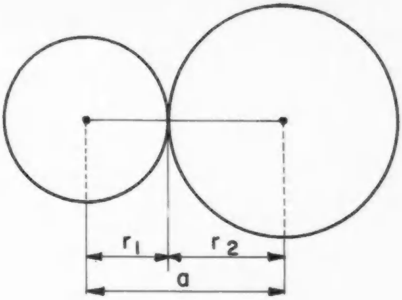


Fig. 14
Diagram illustrating two atoms (assumed spherical) in contact. The distance *a* is measurable, and is apportioned between the two atoms to give the individual radii, r_1 and r_2.

van der Waals, Covalent and Ionic Radii

"Fortunately, the chemist has at hand a great many values of the distance *a* between various atoms. Examination of them shows that three sets of radii can be established from which values can be obtained to agree with observed facts. One set of radii can be used in calculating the distance between an atom in one molecule and the nearest atom in another molecule, when the two molecules are in contact; these are called the van der Waals' radii after the Dutch chemist who did much of the work in this field. A second set consists of radii to be used in calculating the distance between atoms bound together by a non-polar covalent bond; these are called the covalent bond radii. Since only bonds between atoms of the same kind are strictly non-polar, calculation of the actual distance between two different atoms bound by a polar covalent bond requires the application of a correction; this correction depends upon how polar the bond is. The third set of radii are those to be used in

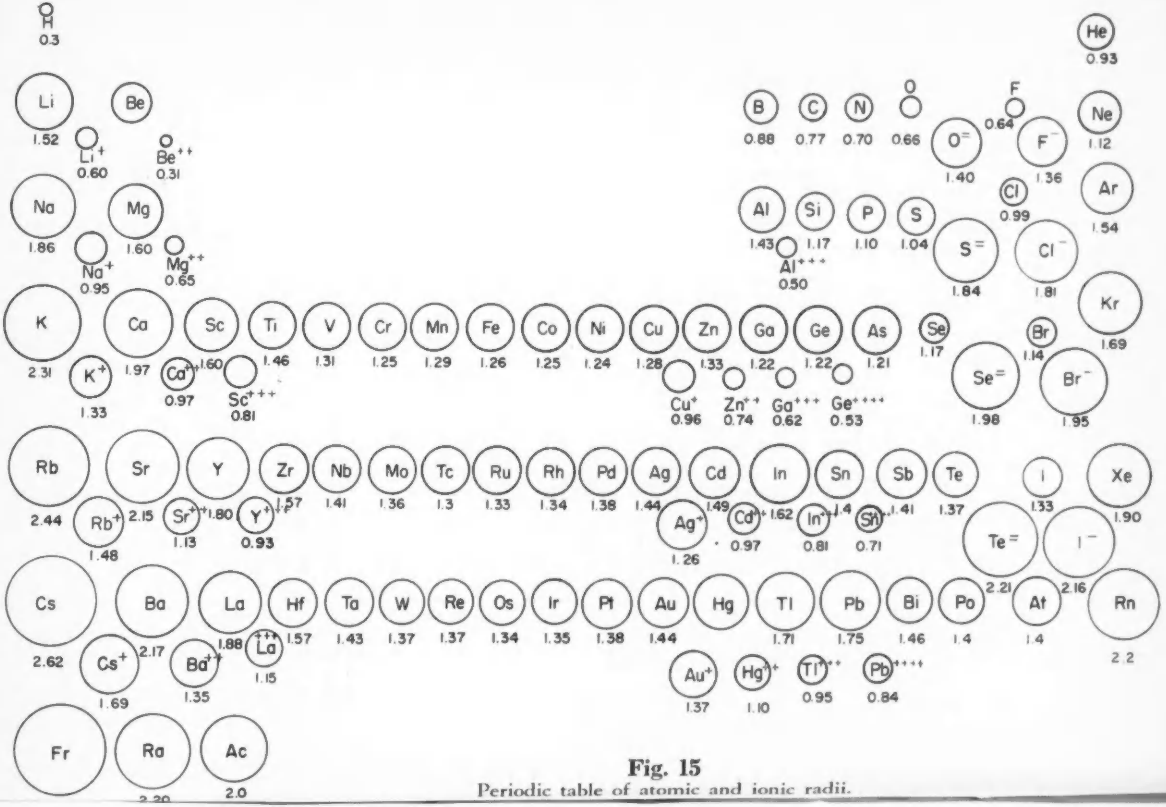


Fig. 15
Periodic table of atomic and ionic radii.

calculating the distance between ions; these are called the ionic radii. These again require modifications depending upon the number of ions of opposite charge in their neighborhood. Only in the case of the distance between two like atoms can we be sure that we have divided *a* correctly into r_1 and r_2; here we give ½ *a* to each atom. Application of consistent principles to the data permits the assignment of sets of radii, which, when used in accordance with prescribed rules that seem reasonable, give values of *a* that are consistent with the facts. We therefore argue that these values are in fact correct, and we use them with confidence.

"It should be emphasized that many values of quantities in science are based upon this principle of consistency with the facts. Oftentimes no one measurement is sufficient to establish it with certainty. Examination of great quantities of data, however, permit us to build up a skeletal structure which fits so many known facts, which is consistent with so many experimental results, that all reasonable doubt that the structure is in fact the one which occurs in nature is removed.

"Fig. 15 shows the values of the atom sizes as calculated from the covalent-bond radii, and the sizes of ions as determined from the ionic radii. In general, the van der Waals' radius is larger than the covalent bond radius, approaching, for the negative ions, the ionic radius.

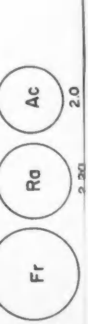
"It is evident immediately from Fig. 15 that the size of the atoms is a periodic function of the atomic number. There is a progressive decrease in size of the atom in each period from I to VII. This is the expected result from the increase in nuclear charge with no change in the number of inner electron shells. The decrease in size results in an increase in ionization potential and decrease in metallic character which has already been noted. In the transition elements of each long period the size does not change appreciably, the increase in nuclear charge being approximately balanced by added electrons in the *d* orbitals. The effect of the increased nuclear charge, however, is sufficient to make the atoms immediately following the transition elements, with an inner shell of 18 electrons, much smaller than atoms in the same period which have one or two electrons over a shell of 8. (Compare for example, silver with rubidium, zinc with calcium, for both the free atoms and the positive ions.)

"Within a family the atoms increase in size as the atomic number increases; this indicates that the enlarging effect of the intervening inner shells is such as to overcome the contractive effects of the increased nuclear charge. This is also reflected in the decrease in ionization potential within families; the electron to be removed is farther away from the nucleus in the heavier atoms of the family, and less energy is required to remove it.

"The lanthanides, which do not appear in Fig. 15, show a slight decrease in size with increasing atomic number. This is accounted for by the increase in nuclear charge without the introduction of intervening shells of electrons, and makes the elements following them smaller than one might have expected on the basis of the changes in the earlier periods. Thus

Fig. 15

Periodic table of atomic and ionic radii.



hafnium is not significantly larger than zirconium, etc. This too is reflected in the values of the ionization potentials, which, for the elements of the sixth period following the lanthanides, tend to be greater than those of the corresponding members of their families in the fifth period. This appears to be the reason why the ionization potential of radium does not agree with the orderly change of ionization potentials in the alkaline earth series. There is a very much greater increase in nuclear charge in passing from barium to radium than in passing from strontium to barium, yet in each case the number of electron shells is increased only by one. This large increase in nuclear charge tends to keep the atom small, and the outer electron is not as easily removed from radium as one might have expected from the trend of ionization potentials observed for the lighter members of the alkaline earth family."

Most ionic compounds are formed by the reaction of a metal with a covalently bonded non-metal. Thus, before these reactions can logically be discussed, attention must be given to the forces which hold metallic crystals together. Accordingly, metallic bonding is considered in Chapter IX. Once the student accepts the possibility that two positively charged nuclei can be held together by the mutual attraction of the nuclei for a pair of electrons, it is a small step to realize that a large number of positively charged nuclei could be held together by the mutual attraction for a large number of electrons. This, crudely stated, is the situation in the metallic bond.

The Metallic Bond

"It is evident that the binding which holds these atoms together must be different from the binding in covalent substances, since the metal atoms do not have nearly enough electrons in the outer shell to form electron-pair bonds with 12 adjacent atoms, nor with 14 (8 + 6). Metal atoms have only a few electrons in their outer shells. However, some general features of the bonding in metals can be inferred from physical properties. Thus most metals are tough. It takes a considerable force to break a metal wire by pulling it. This indicates that powerful attractive forces operate through the body of the metal wire. At the same time the metal wire may be bent without destroying its strength. Most metals are not brittle. Forces between metal atoms must operate even when the metal piece is deformed and the atoms are moved in relation to each other. Therefore, binding in metals requires that there be forces extending out in all directions from each atom. The only source for these forces in metals, as for all forces involved in chemical binding, is electrostatic attraction. The detailed description of the metallic bond has not yet been developed, but a useful picture is one in which the outer electrons of each atom are imagined to be removed to form positive ions and the electrons scattered around among the atoms to act as a smeared-out negative charge which counteracts the repulsion between the positive ions and holds the crystals together.

"It is proper to imagine the electrons as being free to move about in the structure between the ions. The electrons in the valency shell are not attached to any individual ions or pair of ions. They belong to the crystal as a whole, and not to any portion of it. This is true only of the outer electrons; the electrons in the inner shell do remain attached to their individual nuclei and are, for the most part, not concerned in contributing to the metallic binding.

"The importance of the observation that metallic characteristics are shown only by those elements whose atoms have few electrons in the valency shell may be emphasized by considering the structures of the first and last elements in group IV in the periodic table. Carbon forms crystals with the diamond structure, in which each atom is attached by strong covalent bonds to each of four other carbon atoms. The four valence electrons per atom are used in pairing with one electron from each of the other four carbon atoms. Carbon as diamond shows no metallic character. Lead, the last element in group IV, has the characteristics of a metal, and crystallizes in the typical face-centered cubic lattice characteristic of metals. The reason for the difference is that in lead, with the outer electron structure $6s^26p^2$, the two 6s electrons are held tightly to the nucleus by the high nuclear charge, and binding involves only the two unpaired *p* electrons. This decrease from 4 to 2 in the number of electrons available for use causes crystalline lead to be metallic compared to the diamond.

"The effect of number of valence electrons is also shown in the case of tin which forms two different kinds of solid crystals. One of these, known as grey tin, has the diamond structure, in which each tin atom is held by four covalent bonds; crystals of grey tin have most of the non-metallic properties to be expected from such a structure. The other crystal form, known as white tin, has the properties of a metal, it is shiny and a good conductor, and it has a structure which, while not conforming exactly to any of the three crystal structures we have discussed is definitely of a metallic type.

Properties of Metals From Structure

"The structure of metals is responsible for many of the properties such as malleability, ductility, bending, springiness, and toughness. In metals, there is (a) non-directional bonding, (b) empty spaces, and (c) glide planes.

"When the surface of a metal is examined under a microscope, what appears to be a smooth, homogeneous surface will then seem to be a mosaic of crystals, often called grains. The grain boundaries are actually separations of small crystals of the metal. By careful control of temperature in the proper environment, it is possible to grow single crystals of many metals from their melts. Single crystals of metals do not have the same properties as gross pieces of untreated metals. The pure single crystal is softer and has higher thermal and electrical conductivity. Grain boundaries are absent and the ease of passage of electrons is therefore maximum. Tensile strength will be greater in a single crystal because holes and irregularities in the lattice are fewer.

"The single crystal has a lattice structure near the ideal while ordinary metal would entail empty spaces and irregular joining of lattices at the grain boundaries.

"Bending a single crystal will dis-

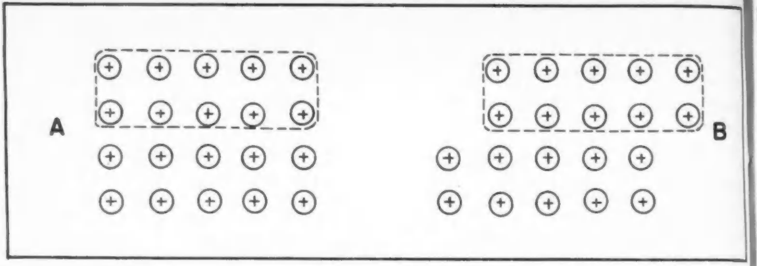


Fig. 16
Forced displacement of ions in a metal along a glide plane.

place some atoms so that new grains are formed. The metal will no longer be a single crystal and will then be harder than it was originally. For the same reason bending an ordinary piece of wire makes it harder at the point of the bend and it is seldom possible to return it to its original shape. Instead it bends in a new place. Working (hammering or drawing) a metal destroys some of the glide planes and makes the metal harder to deform than it was before.

"The structure of metals contributes to the ease with which they may be deformed. To a group of metal ions, one ion looks like its neighbor, and it is possible to shift ions about in the electron 'sea' without disturbing the binding noticeably. Suppose for example, that the group of ions at A in Fig. 16 is moved to position B.

"In the gross picture nothing has been changed except at the crystal edges; in the interior of the crystal the environment of each metallic ion is the same as in the old position. Metallic ions, then, give up old loyalties easily and form new strong bonds easily at the new displaced positions. This is a striking difference between the non-directional bonding of metals and the directed valence in covalent molecules. The displacements in Fig. 16 will also suggest why metals are ductile. Continued slippage along glide planes will allow the metal to be drawn into wire without breaking.

"Figure 17 shows the initial and final states of a deformation, but does not describe the intermediate stages. It must not be supposed that the whole set of ions moves bodily from one place to another simultaneously; rather one ion moves at a time, and the dislocation moves more or less gradually across the crystal. Most crystals, in fact, will be imperfect, in that there will be vacant places in the crystal lattice where ions are missing, or extra planes of ions which disturb the regularity. Deformation of the crystal is then somewhat easier in these cases, because the deformation itself may serve to "straighten out" the crystal pattern along these deformations (Fig. 17).

"The deformation of massive pieces of a metal is more complicated than this, since a large piece of metal is usually made up of many crystals, and part of the changes in shape are con-

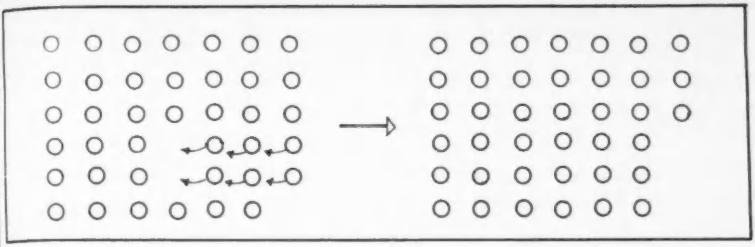


Fig. 17

Migration of metallic atoms in a crystal removes imperfections.

cerned with sliding crystals over each other rather than deforming the crystals themselves.

"Diamonds and covalently bonded interstitial compounds such as tungsten carbide do not bend because the bonding is directional. When the stress is transmitted to the rigid system, there are no glide planes so that layers of atoms cannot be moved over one another.

"Metals generally have high elasticity. If the stress is small, atoms are displaced without moving a whole glide plane and the atoms spring back to their original positions when the stress is removed to restore the perfect lattice. This accounts for elasticity. Further displacement causes bending and the metal does not return to its original shape when the stress is removed.

"Irregularities at grain boundaries are generally points of weakness. Corrosion in metals ordinarily starts at such points. Single crystals are notably less susceptible to corrosive action of the air or of chemicals.

Energy Levels in Metals

"Just as earlier sections of this book have discussed the separation of the energies of electrons in isolated atoms into various allowed energy levels, so also the valence electrons in metal crystals have certain energy levels. The difference between isolated atoms and those in a crystal is that the atoms in a metal crystals are close enough together for the electrons on adjacent atoms to interfere with each other. This means that the energy levels of the individual atoms no longer coincide, but are slightly different. This results in bands of extremely close-spaced energy levels which are characteristic of the crystal as a whole rather than of individual atoms. The several bands may themselves be close together, far apart, or they may overlap each other depending upon the elements in the crystal. Each energy level within a band has space for two electrons, as required by the Pauli exclusion principle, and fills from the lowest energy level upward as enough valence electrons are fed to give the proper number of valence electrons per atom. We can imagine, then, a building up of the electron structure of a crystal in exactly the way we built up the electron configurations of the elements in the periodic table. A difficulty is that the range of energies in a band, the separation of bands from each other, and the possible overlapping of bands, depend upon the arrangement in the crystal as well as upon the element present, so that this building up is not as simple as in the earlier discussion. This point of view can, however, be used to discuss some general features of metallic conductors as compared to insulators.

"Let us consider a crystal of an alkali metal which has one valence electron per atom. Associated with the alkali metal crystal there will be a group of energy bands for the valence electrons, which we might represent, very schematically, as in Fig. 18. Each band has room for two electrons per atom; hence for an alkali metal, the lowest band would be half full, as indicated. Alkali metals are conductors, and we interpret the conductivity by saying that there are a number of empty spaces in the band into which the electrons can move with very little expenditure of energy. The possibility of moving into unoccupied energy levels permits a flow of electrons, which we measure as a current.

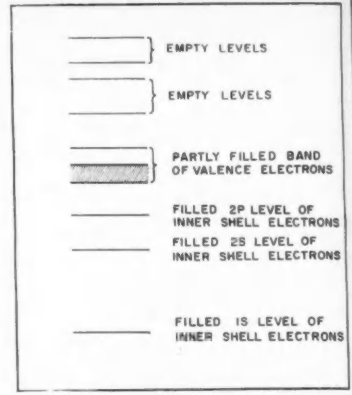

EMPTY LEVELS
EMPTY LEVELS
PARTLY FILLED BAND OF VALENCE ELECTRONS
FILLED 2P LEVEL OF INNER SHELL ELECTRONS
FILLED 2S LEVEL OF INNER SHELL ELECTRONS
FILLED 1S LEVEL OF INNER SHELL ELECTRONS

Fig. 18

Schematic diagram of energy levels in metallic sodium.

Energy Levels in Insulators

"In contrast to the behavior of an alkali metal, an insulator has its energy bands filled with electrons, so that there are no vacant levels available for them to enter. The energy level diagram may be imagined to look like Fig. 19 in which the lower bands are filled, and the energy gap between these and the next band is too great to permit electrons to enter it, and no conductivity results. This is exactly what happens in the case of the diamond. In this substance there are two low-lying bands (one of which is very narrow) each of which will take, per atom, two electrons of opposite spins. These are just filled by the four valence electrons. The next higher levels are much higher, being separated from the lower levels by what is sometimes called a 'forbidden' zone. Ordinary energies are not sufficient to move the electrons across this forbidden zone into the higher levels, and the crystal does not conduct. Note that according to this theory the electrons in the diamond also belong to the crystal as a whole rather than to any pair of carbon atoms and move about in the crystal. They are not able to act as conduction electrons, however, because there are no empty energy levels available into which they can be transferred."

Chapter X presents an extended discussion of ions and their reactions. An attempt is made to explain metal-nonmetal reactions in terms of the changes which take place in their electronic environment. Oxidation-reduction reactions are treated in terms of the free-energy changes involved. There seems to be no advantage at this stage in the introduction of the concept and measurement of standard electrode potentials. The oxidation-number method of bookkeeping for balancing oxidation - reduction equations is employed.

In Chapter XI the concept of covalent bonds is extended to the situation in which the shareholders in the electron pair have unequal electronegativity and, hence, the bond is polar in character. The physical properties associated with polar bonds are explored in some detail in terms of the second period hydrides. The chemical consequence of polar bonds is illustrated with the reactions of the hydrogen halides and halogens themselves.

In the past a number of different classes of reactions have been found useful. These include such familiar groups as oxidation-reduction and acid-base reactions. Any systematic attempt to base the understanding of chemical reactions on electronic and structural considerations does not require these classifications. The approach this course adopts is capable, in principle, of comprehending all chemical reactions. Nevertheless it probably is wise to introduce the student to the terminology and typical examples to show how they fit into the general picture. It is clear that the introduction of these special reactions does not necessitate the introduction of any new principles.

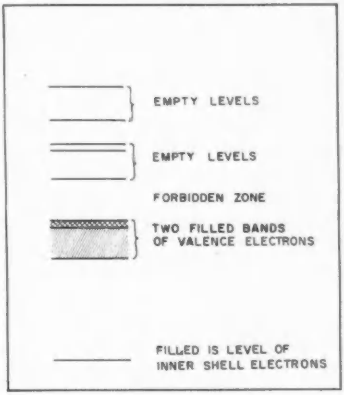

EMPTY LEVELS
EMPTY LEVELS
FORBIDDEN ZONE
TWO FILLED BANDS OF VALENCE ELECTRONS
FILLED IS LEVEL OF INNER SHELL ELECTRONS

Fig. 19
Schematic diagram of the energy levels in a diamond.

Acid-base chemistry and equilibria comprise Chapter XII. This section begins with the electronic or Lewis theory of acids and bases. It is then pointed out that the Arrhenius (H^+ - OH^-) theory or the Bronsted-Lowry (proton donors or acceptors) theory, although less general, may be useful in certain situations. Equilibrium constants, pH, and titration are discussed. The stoichiometry of reactions is developed from atomic and molecular weights, and hence equivalent weights and normality are not introduced. The level of the material is illustrated by the following discussion of acid strength:

Potential Acids of Type MOH

"When a hydride such as HCl or H_2S acts as an acid in the presence of water (or other proton acceptor) the bond which is ruptured is already more or less polar and this rupture is helped by the release of much energy in the formation of the solvated proton-nearly 300 Kcal/mole in the case of

$$H^+ + H_2O \rightarrow H_3O^+$$

"Suppose for the sake of argument that the proton is bonded to M *through oxygen*. This is the case in what we may call hydroxides of the type M-OH. It is possible to say, very roughly, that the hydroxides of metals tend to be basic while those of non-metals tend to be acidic. Let us see why this should be so.

"Evidently the bond in M-O-H may break in either of two ways:

$$\underset{\text{Type A}}{M + O - H} \qquad \underset{\text{Type B}}{M - O + H}$$

The nature of atom M will determine the relative strengths of the M-O bond and the O-H bond. We may assume for the moment single bonds are shared electron pairs with varying degrees of polarity, so that we can use the varying electronegativity of the atom M as a basis for deciding the attraction or repulsion of electron pairs along these bonds. From this we shall be able to judge whether dissociation into ions will follow Type A or Type B. First let us consider the two extreme cases: the hydroxides of sodium and chlorine. Sodium (at No. 11) is a typical metal. The single 3s electron of the relatively large sodium atom is very loosely held as is shown by its low ionization energy of 5.14 e.v. and by its standard electrode potential of +2.7 volts for the reaction

$$Na \rightarrow Na^+ + e^-$$

in solution. Evidently sodium is a strong *electron donor* and its electronegativity of only 0.9 reflects this. We learned earlier that if the difference between the electronegativities of two bonded atoms is greater than 1.7 the bond will tend to be ionic. Since the electronegativity of oxygen is 3.5 we can see that in Na-O-H the Na-O bond will certainly be ionic so that the dissociation of Na-O-H will follow Type A and the substance sodium hydroxide will be a *base*, $Na^+ \; OH^-$.

"The hydroxides of other typical metals will behave similarly, the size and electronegativity of the metal atom determining the strength of the base, within a group. Thus KOH is stronger than NaOH and LiOH is weaker, though the difference is slight and cannot be determined in water. All alkali metal hydroxides are completely ionized in both the solid state and in water solution.

> *Exercise:* From the argument given for the relative strengths of the hydrohalogen acids (Sect. 12-5) suggest a solvent for determining the relative base strengths of KOH, NaOH, and LiOH.

"It is not hard to predict what should happen as we progress across the third period from sodium to chlorine. In Cl-O-H the atom M (i.e. Cl) is that of a typical non-metal. This means that M is small and has a great affinity for electrons (electronegativity of Cl = 3.0). Hence the Cl atom exerts a strong pull on the electrons which bond it to O, and as a result of this the electron pair bonding O to H is pulled closer to the oxygen. From the standpoint of electronegativity difference (3.5 - 3.0) Cl and O should remain covalently bonded, while the drift of the electron pair from H to O may cause dissociation into OCl^- and H^+.

$$HOCl \rightleftharpoons H^+ + OCl^-$$

"Thus the dissociation to be expected here is of Type B, and Cl-O-H is classified as an acid, hypochlorous acid, whose formula is usually written HoCl. Hypochlorous acid is quite weak ($K_i = 10^{-9}$) and is not in itself very important.

"Within the limits of the third period we have seen the chemical properties of MOH change from those of a strong base NaOH (Group I), to those of a weak acid, HOCl (Group VII). We shall not examine the intermediate compounds more closely, but we would expect a gradual change in properties, i.e., gradually increasing acidity as M becomes more non-metallic. Evidently some hydroxides would be quite intermediate in character, with little difference in strength between the M-O bond and the O-H bond. In such cases the type of ionization might be determined by the surroundings in which the molecule MOH was placed. Limiting our discussion to the 'water system' of acids and bases we can see that presence of excess H_2O^+ might force MOH to act as a base, while excess OH^- ion would cause MOH to act as an acid. Hydroxides which show such behavior (e.g., $Be(OH)_2$, $Al(OH)_3$, $Zn(OH)_2$) are said to be amphoteric:

$$\underset{\text{base}}{Zn(OH)_2} + \underset{\text{acid}}{2H_3O^+} \rightarrow Zn^{++} + 4H_2O$$

$$\underset{\text{acid}}{Zn(OH)_2} + \underset{\text{base}}{OH^-} \rightarrow Zn(OH)O^- + H_2O$$

$$Al(OH)_3 + 3H_3O^+ \rightarrow Al^{+++} + 6H_2O$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_2O^- + H_2O$$

The polar character of covalent bonds is extended in Chapter XIII to include hydrogen bonds in water and similar substances. The mechanism of solubility is examined from the viewpoint of the polarity of the molecules present and the dielectric constant of the solvent. Hydration and hydrolysis are examined.

The last four chapters are currently in very rough draft, but their general content can be illustrated by the introductory material in Chapter XIV.

"For the next four chapters we will turn our attention to one of the great simplifying principles of the study of chemistry — the properties of a functional group. Actually we made a start in that direction when we examined the behavior of a series of compounds in which the structure M-OH -OH, and the central atom M. We appeared. But there were two variables in M-OH, the functional group are still interested in the two variables but instead of looking at the effect of changing M on the properties of OH, we will now probe a little farther into the possibility of having M remain constant but vary the environment around M while OH is attached. That is, we will ask what happens to the properties of the functional group, OH, when the other bonds attached to M vary. The particular atom, M, in which we can make the widest variation in other bonds attached to it is carbon. Carbon is unique in forming stable bonds with other carbons and the environment can be changed considerably even while OH still remains attached.

"To examine carefully the meaning and the implications of the nature of a functional group, we will carry out reactions on it to see how it can be replaced. Of necessity this will introduce other functions so in fact we cannot study one functional group in isolation. The study will be limited to Cl and OH for the most part in various situations.

"What we expect to accomplish is to show the power of this method of study for tackling the job of learning the properties of a million compounds of carbon. The task would obviously be hopeless if we tackled compounds individually. The method of studying the properties of functional groups in organic chemistry was first used effectively in a textbook by Ira Remsen before 1890. Until about three years ago textbooks in this field followed his unifying principle almost religiously.

"Some of the chemistry of the OH group has already been discussed in connection with acid-base theory (Chapter XII) and the properties of HOH was the subject of Chapter XIII. The hydroxyl ion is the strongest base known in water solution and its chemistry need not be repeated here. In covalent compounds the properties of the M-OH bond will depend on the character of M. When the difference in electronegativity between oxygen and M is less than 1.7, the O-H bond is often the more easily broken and the substance is acidic (Sect. 12-6) especially if oxygens are cumulated on M in $O_mM(OH)n$.

Parent Hydroxy Compounds

"How many OH groups may be placed around a given atom? If we examine the second and third rows in the periodic table, the following parent compounds can be written on the bold assumption that each outer electron could pair with one electron from oxygen in the OH group:

I	II	III	IV	V	VI	VII
$LiOH$	$Be(OH)_2$	$B(OH)_3$	$C(OH)_4$	$N(OH)_5$	$O(OH)_6$	$F(OH)_7$
$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$P(OH)_5$	$S(OH)_6$	$Cl(OH)_7$

"All the compounds in groups I, II, III are known, none of those in V, VI, and VII is known, and $Si(OH)_4$, but not $C(OH)_4$, is known in Group IV. The assumption is obviously too bold in the case of $N(OH)_5$, $O(OH)_6$, and $F(OH)_7$ since N, O and F do not have more than four orbitals available for bonding, on 2s and three 2p. In P, S, and Cl, the 3d orbitals are available but nevertheless, crowding 5, 6, and 7 hydroxy groups around the central atom is unknown. (Compare PCl_5, SF_6, however.) The first known compounds in these series are what may be called dehydration products from the parent compounds. The nitrogen

$$N(OH)_5 \xrightarrow{-H_2O} [ON(OH)_3] \xrightarrow{-H_2O} \underset{\text{nitric acid}}{O_2N(OH)}$$

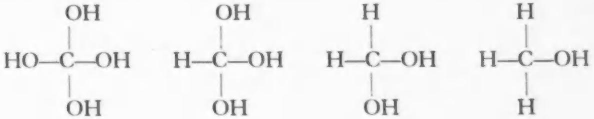
$$P(OH)_5 \overset{-H_2O}{\dashrightarrow} \underset{\text{phosphoric acid}}{OP(OH)_3}$$

acid (nitric) is known in a lower state of dehydration than phosphorus (phosphoric) and this is probably due to the relative sizes of N and P.

"In group IV the first dehydration product (carbonic acid) cannot be isolated although it is known in solution but $Si(OH)_4$ is a known substance.

$$C(OH)_4 \xrightarrow{-H_2O} \underset{\text{carbonic acid}}{OC(OH)_2} \xrightarrow{-H_2O} CO_2$$

"Let us examine another series of compounds that can be derived from $C(OH)_4$ by successive replacement of OH groups by H. One effect is the change in oxidation number if we assume that a C-H bond gives carbon an oxidation number -1 while a C-O bond gives it an oxidation number of $+1$. Although only the last of this series is known, dehydration products



$$\begin{array}{cccc} HO\text{—}\overset{OH}{\underset{OH}{C}}\text{—}OH & H\text{—}\overset{OH}{\underset{OH}{C}}\text{—}OH & H\text{—}\overset{H}{\underset{OH}{C}}\text{—}OH & H\text{—}\overset{H}{\underset{H}{C}}\text{—}OH \\ +4 & +2 & 0 & -2 \end{array}$$

of the other three are known: $CO(OH)_2$, carbonic acid; $HCO(OH)$, formic acid; H_2CO, formaldehyde; CH_3OH, methyl alcohol."

The laboratory part of this course is at least as important as the textual material. Because of the unique format completely new experiments are needed. Detailed directions are kept to a minimum although extensive pre-laboratory discussions are frequently useful. The students are encouraged as much as possible to work out their own procedures. The type of experiments presently in the course can best be illustrated by considering several examples.

In the text, the physical and chemical characteristics of substances are discussed. This includes a consideration of the properties of various compounds in terms of their structure. In some cases, one finds that two substances of approximately equal formula weight might have quite different physical properties. This difference is due to the forces either between the atoms in a molecule or between the molecules themselves. To study the relationship between these forces and physical properties, the students are given a problem involving the determination of the degree of polarity of a group of unknown compounds.[5] These compounds can be arranged in the order of their relative degree of polarity by determining the actual solubility of each unknown compound in different solvents. By using solvents which have different degrees of polarity themselves, the students can establish the relative degree of polarity of the group of unknown compounds. In addition, the students can discuss

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[5] Laboratory, C.B.A.C., Volume I, Experiment 6, Degree of Polarity.

the possible types of chemical bonds which could be present in their unknowns.

In both the class and laboratory work of the C.B.A. course, the significance of chemical equations is stressed. This includes not only the customary consideration of the various notations used in chemical equations but also the consideration of the nature of the reactants and the products. Hence, it is possible for the students to visualize a written reaction as they would observe it in the laboratory. At the same time, the students can carry out a reaction in the laboratory and on the basis of their observations write the appropriate chemical equation for the reaction. In the experiment dealing with halogens,[6] the students obtain experimental evidence which is used to defend or attack a series of statements. One statement which the students are asked to consider is: "The reaction of phosphoric acid with potassium iodide is a better method for preparing hydrogen iodide than the reaction of concentrated sulfuric acid with potassium iodide." By doing each of these reactions in the laboratory, the students can observe the various changes which occur. On the basis of these observations, they decide whether the statement is justified. If it is not, they cite specific experimental evidence to prove their point. To do this, the student must be familiar with the nature of hydrogen iodide, sulfuric acid, phosphoric acid, and potassium iodide as well as with other products which might be formed in this reaction. Some of the other statements presented in this experiment include: "Bromine is more soluble in carbon tetrachloride than in water." "The free energy changes of the reactions of bromide ion with concentrated sulfuric acid and of chloride ion with concentrated sulfuric acid indicate that bromide ion will react with sulfuric acid but chloride ion will not react."

In the course, considerable attention is centered on how and why substances undergo various chemical reactions. This requires an understanding of the nature of each of the substances present in a given reaction system. The students conduct several laboratory investigations of this nature involving different chemical reactions. In one of these, the students are given the problem of investigating the reaction of an acid and a metal.[7] Some of the questions which are raised with the students include: What chemical species are involved in the reaction? What is the actual role of the acid in this reaction? What effect does water have on this reaction? This problem is approached in the laboratory by determining the time required to collect a given volume of hydrogen obtained by reacting a constant weight of acid with a constant weight of metal in the presence of varying amounts of water. By using these experimental data, the students can discuss some of the various factors which influence the reaction of a metal and an acid.

This course is in the nature of an experiment and the material here represents only a first draft. Experience with about 800 students in the nine high schools involved on a formal

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[6] CHEMISTRY, C.B.A.C., Volume II, Experiment 13, Chemistry of the Halogens and Halogen Compounds.

[7] CHEMISTRY, C.B.A.C., Volume II, Experiment 17, Rates of Reaction.

basis in the program and two college classes and three high schools using the material on an informal basis has indicated the overall soundness of the approach and the direction in which the extensive rewriting must take.

So far experience seems to bear out our expectation that this course, although somewhat demanding, is understandable and of real interest to the average students electing to take chemistry in the trial schools. An examination program is being developed to obtain more systematic information about what can be achieved by students in this course.

Supplementary reading material is being collected for students and teachers who wish to go beyond the text.

The teachers and high schools selected to take part in this program are:

Arnold E. Bereit, Central High School, Phoenix, Arizona.

Kenneth E. Borst, Leonia High School, Leonia, New Jersey.

James V. DeRose, Chester High School, Chester, Pennsylvania.

Richard L. Miller, Los Angeles High School, Los Angeles, Cal.

Henrietta A. Parker, Shortridge High School, Indianapolis, Indiana.

Robert J. Shewbert, Grant High School, Portland, Oregon.

Wendell H. Taylor, The Lawrenceville School, Lawrenceville, N. J.

Paul H. M. Westmeyer, University High School, Urbana, Illinois.

Harold V. Wik, Sunset High School, Beaverton, Oregon.

Special mention should be made of the contribution of Professor Leallyn B. Clapp of Brown University to this endeavor. Much of the success of the project is due to his total preoccupation with the course during his stay at Earlham College during the past semester.

Einstein's Relativity Theory Confirmed

➤ YEAR-LONG TESTS, believed the most precise yet made, have confirmed preliminary results by the same method that Einstein's special theory of relativity is correct.

The experiments showed no measurable variation in frequency of radio waves radiated by ammonia molecules as the earth moved around the sun during a year. Einstein's special theory postulated that the velocity of light, 186,000 miles a second, is independent of its frame or reference or of the motion of the light source itself. It also applies to radio waves, which travel at the speed of light.

Results of the experiments, conducted at Columbia University at the suggestion of Nobel Prize winner Dr. Charles H. Townes, are reported in *Nature*, a British scientific publication. His associates found that, at most, less than one-thousandth of the earth's velocity around the sun could affect the speed of light propagation.

High precision of the tests was possible by using two masers. The coined word maser stands for "microwave amplification by stimulated emission of radiation." Previous experiments have confirmed Einstein's theory but not as precisely as the present test.

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New Phthalic Anhydride Plant Planned

➤ REICHHOLD CHEMICALS, INC. is completing engineering plans for the construction of a new phthalic anhydride plant at Newark, Ohio, with 60,000,000 pounds production capacity a year.

Situated on a 70-acre site, which was purchased by RCI this past spring, the new plant should be in production during late 1961.

In addition, necessary raw materials have been guaranteed and secured for use in production of phthalic at this site.

The construction of this facility is in line with RCI's current expansion program and it brings to four the number of company plants producing phthalic in the United States. Other plants are situated in Detroit; Azusa, California, and Elizabeth, N. J.

Bulletin Prepared on Potassium And Sodium-Potassium Alloys

➤ DETAILS on the chemistry, properties, and applications of sodium-potassium alloys (NaK) and potassium are provided in a technical bulletin prepared by MSA Research Corporation, Callery, Pa.

The eight-page brochure suggests numerous applications for sodium-potassium alloys, including use as a heat exchange fluid in atomic reactors or high-temperature processes. Chemical advantage of NaK are also listed.

The chemistry of organic derivatives is outlined with respect to synthesis, reactions, and yields. Various catalytic and inorganic reactions involving sodium-potassium or potassium compounds are also summarized.

Information is presented on shipping, handling, and purity of the two materials, which have been produced on a tonnage basis by MSA Research Corporation since 1940.

The bulletin, MSAR 59-120, is available on request from the Commercial Division, MSA Research Corporation, Callery, Pa.

Borden Chemical Releases Non-toxic Adhesive Data

➤ THE AVAILABILITY of a new list of approved non-toxic adhesives for food packaging applications has been announced by The Borden Chemical Company. The list includes a series of resin based emulsion glues specially designed for convolute and spiral-wound food containers such as used for hot and cold beverages, meats, condiments, frozen foods, dairy products, bakery goods, drinking straws, folding cartons and paper laminating.

Food clearance data from independent testing laboratories are available upon request. All Borden non-toxic adhesives are provided in a wide range of setting speeds in ready-to-use form. Five gallon trial quantities are also being offered. For further information write Department H, The Borden Chemical Company, 350 Madison Avenue, New York 17, N. Y.

Science Talent Search
Project Report

Chemistry of Non-Aqueous Solutions

by Joseph P. Straley
Chapel Hill High School, Chapel Hill, North Carolina

Joseph Straley, at the age of 18, is a winner of the 19th Science Talent Search. He hopes, on graduation, to study mathematics or chemistry at Harvard, and eventually to do pure research in one of these fields.

Introduction

➤ Modern inorganic chemistry is based on a water solvent. All inorganic analysis schemes are based on the water solubilities of the salts of the element tested for. The purpose of this project is (1) to show that the water system is not unique, (2) to discuss the properties of a general solvent system, (3) to explore the solvent system based on ethyl alcohol, and (4) to discuss the advantages of non-aqueous solution systems.

The Water System

The water base is not essential to chemistry. Its origin lies in the fact that water is available, that it is virtually the only common liquid, and that our world has a water-based chemistry. The "chemicals" used by the early chemist were the common substances — anything found in the kitchen or around the house and the easily obtained minerals, such as salt, saltpeter, and vinegar. All of these were soluble in water because they were part of the world's water-based chemistry: salt had to dissolve in water to be used to season soup, and saltpeter was found in deposits formed by water. Because few of these compounds dissolve in goose-grease, turpentine, the alchemist soon came to believe that water was the only useful solvent. Yet water is not the only possible solvent, as is demonstrated by Experiment 1.

The General Solvent System

A solvent system, as referred to here, consists of a solvent in which three kinds of reactions — synthesis, single-displacement, and double-displacement — can take place and the reactions between pairs of reagents. Several things are necessary for the general solvent system. Compounds dissolved must ionize to some extent. To meet this requirement the solvent itself must be ionizable. This excludes, for example, bromine as a solvent unless it assumes the form $(\mathrm{Br}^{+++++++})$, $7\ \mathrm{Br}^{-}$ -bromine bromide. Curiously, this last condition is not desirable: a highly ionized solvent would not be suitable because the excess of positive and negative ions would have undesirable effects, due to Le Chatalier's principle. Molten sodium hydroxide would tend to form sodium compounds and hydroxides in solution in a process analogous to hydrolysis in water. This problem is significant even in water reactions: some compounds, such as carbides, hydrides, and ethoxides, decompose in water to form hydroxides because the compounds formed by hydrolysis (methane, hydrogen gas, and ethyl alcohol) ionize even less than water.

It is necessary to have a number of chemicals soluble in the solvent, though, of couse, not all of them if one intends to have double-displacement reactions go to completion.

In a hypothetical solvent of the form A^+B^- any compound having A^+ ions is considered an acid, and any compound having B^- ions is called a base.[1] [2] In a system using fused ammonium carbonate as a solvent, ammonium chloride is an acid; sodium carbonate, a base. Processes in the general system are largely the same as in the water system: desired chemicals are produced and unknown chemicals identified by suitable double-displacement reactions.

The Ethyl Alcohol System

To test these theses the system of ethyl alcohol was investigated. This solvent conforms to the criteria presented for the general solvent system in the preceding section, was readily available, and was well covered in the literature. The proof that the solvent meets the necessary requirements is amply given by Experiment 1.

The solvent used here was frequently 95% ethyl alcohol or even denatured alcohol. The presence of the water was found to have no observable effects on the experiments. Absolute alcohol was used to verify this fact and in experiments where water was undesirable.

The exploration of the system is best summarized by Table 1, which is a simple solubilities chart. The figures designated by light numerals come from the literature [3] [4] [5] principally the *Handbook of Chemistry and Physics*; those set in bold numerals from personal experimentation. Unfortunately, the results so obtained did not always correlate with those of the *Handbook*. Some of these discrepancies can be blamed upon experimental error, although this did not seem to be the case for magnesium and chromium sulfate. There may be some disagreement in the meaning of the term, "soluble." A substance was called soluble when a substantial amount of it could be made to stay in solution.

Solubility was tested by several methods. When a substance could be obtained or prepared in a fairly pure state, the solubility was tested by evaporation of a sample of alcohol which had been shaken with the compound. If a compound imparted a tint to the solvent, the color was taken as sufficient proof of solubility. Magnesium sulfate, sodium sulfide, chromium sulfate, and aluminum chloride were tested by this method.

A large number of the tests were conducted by means of double-displacement reactions. Experiment 2 gives a general outline of the procedure.

Advantages and Disadvantages of Non-Aqueous Solution Systems

Two advantages of non-aqueous solutions suggest themselves immediately: some ions could be precipitated more easily than in water, and compounds unstable in water could be prepared.

Sodium, potassium, and ammonium salts are precipitable in some systems, among them that of ethyl alcohol. The qualitative analysis scheme for alcohol

TABLE I

Table of Solubilities in Ethyl Alcohol

	$C_2H_5O^-$	Br^-	$CO_3^{=}$	ClO_3^-	Cl^-	CrO_4	OH^-	I^-	NO_3^-	$S^{=}$	$SO_4^{=}$
Al^{+++}	**S**	S	I	—	**S**	**S**	I	S	S	**I**	**I**
NH_4^+	S	S	I	I	I	I	**S**	S	S	S	I
Ba^{++}	I	S	**I**	I	I	—	I	I	I	S	**S**
Ca^{++}	I	S	**I**	S	**S**	S	**I**	S	S	**I**	**I**
Cr^{++}	I	S	**S**	—	I	—	**I**	—	**S**	**I**	I-**S**
Co^{++}	S	S	**I**	S	S	**I**	**I**	S	S	**S**	I
Cu^{++}	I	S	**I**	S	S	**S**	**I**	—	S	I	I
Fe^{+++}	**S**	S	**S**	—	**S**	**S**	**S**	—	**S**	**I**	S
Fe^{++}	**S**	S	—	—	**S**	**S**	**I**	S	**S**	S	I
Mg^{++}	S	S	—	S	**S**	**S**	**I**	S	S	**S**	S-**I**
Hg^+	**Sl.S.**	I	I	S	**I**	I	**I**	I	S-**Sl.S**	**I**	**I**
Ni^{++}	I	S	**I**	—	S	**I**	**I**	S	**S**	**I**	I
K^+	S	I	I	I	P	I	**S**	S	I	**S**	I
Na^+	I	I	I	S	I	**S**	**S**	S	**S**	**S**	I
Zn^{++}	I	S	—	S	**S**	**I**	**I**	S	S	**I**	I

LIGHT LETTERING — Data from the literature.
BOLD LETTERING — Conclusions from personal experimentation.

S - Soluble I - Insoluble Sl.S - Slight Soluble

is given in Experiment 3. This particular experiment is rather interesting for the simplicity of both reagents and laboratory procedures involved.

The advantages of simple methods of synthesis of water-unstable compounds are obvious: oxides could be as simply prepared in the laboratory as sulfides. Metal carbides, hydrides, and azides could be made without heat or pressure if a solvent could be found. These experiments were beyond the scope of this study due to the fact that, of the oxides and carbides available, there was none which would dissolve and which did not react with the solvent. Another experiment of this type which was tried successfully is the preparation of an ethoxide. Sodium ethoxide (CH_3-CH_2ONa) can be prepared by treating small quantities of sodium metal with ethyl alcohol.[6] This compound is unstable in water, decomposing into sodium hydroxide and ethyl alcohol.[7] It is, however, soluble in alcohol, so that other ethoxides can be obtained easily (Experiment 4).

The obvious disadvantage of nonaqueous chemistry is the difficulty of transfer of the dissolved chemicals from one solvent to another. The problem is more difficult with water and alcohol than it is with immiscible solvent pairs. In the latter case an appreciable sample of the dissolved salt can be obtained by shaking the solution and the new solvent together if the solubility in the new solvent is fairly high.

Summary

Many solvents can be used as a medium for chemical reactions. There are possible advantages of basing a chemistry on a non-aqueous solvent. The nature of the general solvent system has been discussed, and the findings have been applied to the chemistry of alcohol solutions.

Experiment 1: Double-displacement Reactions in Alcohol

Preparation: Alcohol solutions of sodium hydroxide and ferric chloride are prepared.

Hypothesis: The sodium hydroxide and the ferric chloride will react in the alcohol:

$$3NaOH + FeCl_3 \rightarrow Fe(OH)_3 + 3NaCl \downarrow$$

The solubilities of the compounds are given in the *Handbook of Chemistry and Physics.*[3]

Process: The two liquids are mixed together.

Verification of hypothesis: A light-colored precipitate results, and the liquid remains brown. The precipitate is washed with alcohol, leaving a salty-tasting white crystalline solid, sodium chloride.

Experiment 2: Determination of Solubility of Zinc Hydroxide

Preparation: Prepare alcohol solutions of sodium hydroxide and zinc nitrate.

Known: That sodium hydroxide, zinc chloride and sodium nitrate are soluble in alcohol (from Table 1).

Hypothesis: The zinc hydroxide prepared

$$2NaOH + Zn(NO_3)_2 \rightarrow 2NaNO_3 + \underline{Zn(OH)_2}$$

will precipitate if it is insoluble in alcohol.

Process: The two liquids are mixed.

Result: A white precipitate is formed, from which it is concluded that zinc hydroxide is not soluble in alcohol.

Experiment 3: A Qualitative Analysis Scheme for Na^+, K^+ and NH_4^+

Given: An alcohol solution containing sodium, potassium, and ammonium ions.

Procedure:

A. Precipitate K^+ with nitric acid. Filter.

B. Precipitate NH_4^+ with chromic acid or ferric chromate. Filter.

C. Precipitate Na^+ with sulfuric acid.

Experiment 4: Preparation of Calcium Ethoxide

Preparation: Make solutions of anhydrous calcium nitrate and sodium ethoxide in absolute alcohol.

Hypothesis: Calcium nitrate and sodium ethoxide will react:

$$Ca(NO_3)_2 + 2CH_3CH_2ONa \rightarrow + \underline{(CH_3CH_2O)_2Ca}$$

Process: The two liquids are mixed.

Result: A gummy white precipitate of calcium ethoxide is formed.

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4. *A Dictionary of Chemical Solubilities, Inorganic*, ed. Arthur Comey and Dorothy Hahn (New York: Macmillan Co., 1921).

5. *Handbook of Chemistry*, ed. Norber Lange (9th ed.; Sandusky: Handbook Publishers, Inc., 1956).

6. James Conant, *The Chemistry of Organic Compounds* (revised ed.; New York: Macmillan Company, 1939) p. 19.

7. *Ibid.*, p. 20.

√ Chemistry Quiz √

Directions: Mark the answer you think is *most nearly correct.* Answers are on page 44.

A. At the lowest known temperature (almost absolute zero), every element and every compound except one is a solid. Which one is it?
   1. helium
   2. hydrogen
   3. nitrogen
   4. oxygen

B. The term "molecular engineering" refers to
   1. control of chemical reaction through electronic computers
   2. designing of nuclear reactors
   3. developing chemical compounds to fit specific needs
   4. developing industrial materials from farm crops

C. Which one of the following statements is *least* true of lithium?
   1. It is a seldom exploited byproduct of aluminum production.
   2. It is useful in metal refining.
   3. It is useful in the preparation of special lubricants.
   4. It will float on gasoline.

D. Yttrium's advantage in the nuclear field is "its relatively low thermonuclear cross section." This means that
   1. it has less resistance than many other materials to the passage of neutrons needed to sustain a nuclear reaction
   2. it is highly resistant to the passage of neutrons
   3. it takes very little of this material to contain an active reactor cell
   4. its melting point is high enough to withstand reactor temperatures

E. Which of the following has the *least* in common with the other three?
   1. anthracene
   2. ethylene
   3. toluene
   4. xylene

Complete copies (with answers and norms) of many previous Science Talent Search examinations are available at 15c each from Science Service, 1719 N St., N.W., Washington 6, D. C.

For the Home Lab

Benzoic Acid

by Burton L. Hawk

➤ Benzoic acid is best known as a preservative. No doubt you have seen it or its compounds listed as an ingredient on the labels of many food products. It is also used in dyes and in the manufacture of other organic chemicals. In medicine it functions as a fungicide and is particularly helpful in the treatment of Athlete's Foot and other fungus infections.

Benzoic acid is found in nature in most berries, especially cranberries. It is excreted in the urine of most animals as hippuric acid. Until 1877, benzoic acid was obtained from the urine of horses and cattle by hydrolysis of the hippuric acid. Fortunately, synthetic methods of preparation have eliminated this crude procedure. It is made now by treating molten phthalic anhydride with steam and catalyst, by the hydrolysis of benzotrichloride, or by the oxidation of toluene.

Preparation

In the home laboratory, the simplest method to prepare benzoic acid is by the oxidation of benzaldehyde using the Cannizzaro Reaction. Of course, benzoic acid is more readily obtainable than benzaldehyde so it would be more sensible to prepare benzaldehyde from the acid. But, that's beside the point; since this is an article on benzoic acid, we must make benzoic acid.

First, to assure success of the experiment, the benzaldehyde must be freshly distilled. Be careful in performing this operation, as benzaldehyde tends to bump and spurt when it boils. It might be a good idea to add a few glass beads in an effort to promote smoother boiling. About 7 cc. will be required.

In another container dissolve 6 grams of potassium hydroxide in 5 cc. of water, heating if necessary. This is a strong alkali so be most careful not to spill any of it on your skin or clothing. Cool the solution and add it to the 7 cc. of freshly distilled benzaldehyde in a small flask. Stopper the flask securely with a cork and shake the contents vigorously until a smooth milk-like emulsion is obtained. Then set the flask aside and allow it to stand quietly for about 24 hours. At the end of this time a white precipitate of potassium benzoate will separate out of solution.

Carefully filter off the precipitate and dissolve it in water. Use as much water as necessary to dissolve all of it. In another container mix 10 cc. of hydrochloric acid with 10 cc. of water and add a small quantity of cracked ice. Stirring constantly, slowly add the potassium benzoate solution to the cool hydrochloric acid solution. Benzoic acid is precipitated. Filter it off and dissolve in hot water. On cooling the benzoic acid recrystallizes in fine white needles.

In a test tube, add a small quantity of finely powdered manganese dioxide to a dilute solution of sulfuric acid. To this, add about 10 drops of toluene. Stopper the tube and shake thoroughly. Remove the stopper and smell cautiously. Can you detect the almond-like odor of benzaldehyde? This is formed as a result of the oxidation of the toluene. Theoretically further oxidation should produce benzoic acid. However the direct oxidation of toluene to benzoic acid is very slow under home laboratory conditions.

Usually, benzyl chloride is used as the starting point. This material is hydrolyzed to benzyl alcohol and the latter oxidized to benzoic acid.

Reactions

If you were with us last month, you will remember that salicylic acid forms phenol when it is heated with soda lime. In a similar manner, benzene can be prepared from benzoic acid. In a hard dry test tube (Pyrex), place equal quantities of benzoic acid and soda-lime. Heat, gradually at first, and ending up quite strongly. Smell *cautiously* at the mouth of the tube. You should be able to detect the odor of benzene. If you do not have soda-lime, substitute equal quantities of sodium hydroxide and calcium oxide instead.

Add a solution of ferric chloride to a solution of benzoic acid. A buff colored precipitate is obtained. Since benzoic acid and salicylic acid are similar in appearance, this test can be used to tell them apart. Ferric chloride added to salicylic acid forms a violet coloration, (again, from last month).

As a confirmation test, you can convert the benzoic acid into salicylic; then test for the violet coloration. Add 3 drops of dilute ferric chloride solution, 3 drops of ferrous sulfate solution and 3 drops of hydrogen peroxide to 5 cc. of benzoic acid solution. Watch for the violet color to form.

For a variety on the above test, substitute boric acid solution (5%) for the ferrous sulfate. This time a blue color develops.

As you should have deduced by now, benzoic acid is more soluble in hot water than in cold. In fact, its solubility increases as the temperature of the water increases. It is very soluble in alcohol.

When heated, the crystals melt and the vapor sublimes in the upper cooler part of the tube. The vapor is irritating and will cause coughing if inhaled.

Glycols for Aerosols

➤ GLYCOLS, glycol-ethers, and polyglycols show promise as solvents for pharmaceuticals in aerosol formulations, particularly as substitutes for ethyl alcohol which sometimes causes an undesirable cooling effect or irritating in skin applications.

Logical applications, Dr. P. A. Sanders of Du Pont's "Freon" Products Laboratory told the Chemical Specialties Manufacturers' Association, are topical anesthetics, antiseptics, burn preparations, antibiotic preparations, and similar products for external application. The glycols, because of their relatively low toxicity, also should be useful in formulation of cosmetic items, he said.

Several dozen of the glycols or glycol derivatives have been studied in Du Pont's aerosol service laboratory and results are available to the pressure packaging industry in a new Du Pont technical bulletin. Of particular importance are the data on solubility of the glycols in fluorinated hydrocarbon propellents which will aid aerosol packagers in formulating products containing glycols.

Because many of the pharmaceutical ingredients are insoluble in fluorinated hydrocarbons, such as "Freon" propellents, it has been necessary in the past either to formulate pharmaceutical aerosols as powder sprays or use cosolvents, explained Dr. Sanders. Ethyl alcohol generally has been used as a cosolvent because it not only is completely miscible with the "Freon" propellents but also has adequate solvent powers for the pharmaceutical ingredients.

Tests conducted so far in Du Pont's laboratories indicate many of the glycols are sufficiently good solvents to be substituted for the ethyl alcohol in aerosol formulations or added to ethyl alcohol in sufficient proportion to reduce the alcohol's undesirable chilling or irritating effects.

➤ "IN THE TEEN-AGE SURVEY, *12 were doing homework, 14 were playing records and one was fiddling with a chemistry set!"*

Apparatus Article

The Clinical Gas Partitioner

➤ SIX MINUTES is sufficient time to determine the carbon dioxide, oxygen and nitrogen in blood, serum or respiratory gases, using a Fisher Clinical Gas Partitioner.

This new instrument from the Fisher Development Laboratories is considered to be one of the most important advances in clinical and physiological gas analysis since the Van Slyke technique was introduced a generation ago.

The advantages of the Clinical Gas Partitioner are these:

- It takes less than a quarter the time of a Van Slyke analysis for the same three gases.
- It uses only 0.1 ml of blood or serum, a tenth of the usual sample for a Van Slyke analysis. This small sample size is especially important in work with children or small animals. A 1-ml sample is adequate with respiratory gases.
- Results are reproducible and correlate well with Van Slyke analyses. Carbon dioxide in serum can be measured with a reproducibility of ±1%; blood gases to ±1.5% or better. By using a special gas sampling valve, respiratory gases can be analyzed with a reproducibility of ±0.2%.
- The analysis is automatic. Once the operator injects a blood sample into the reaction chamber, the Clinical Partitioner automatically extracts the dissolved and combined gases, separates them, and measures the amount of each component in the mixture. There is none of the continual manipulation of stopcocks and leveling bulbs that makes a Van Slyke analysis so time-consuming and tedious.
- A permanent record of each analysis is obtained. The Partitioner is used with a strip-chart recorder (not supplied) that plots a chromatogram for each sample. Each "peak" on the chart is produced by a different gas, and the area under the peak is proportional to the amount of that gas in the sample.
- Other gases can be determined. Carbon monoxide gives a peak immediately after carbon dioxide. Carbon dioxide and oxygen *content* and *capacity* can both be measured, depending on the way the sample is handled. Simple modifications in the chromatographic system enable you to get carbon dioxide in 2 minutes, and to analyze for ether and other anesthetics.

Gas Chromatography

The Clinical Gas Partitioner performs its rapid, accurate analyses by the relatively new process known as gas chromatography. This is analogous to the column chromatography that has been so valuable an aid in all branches of biological and biochemical analysis, in which a solvent is used to carry the sample through a column filled with some fine inert powder such as diatomaceous earth. In gas chromatography, an inert carrier gas replaces the solvent. In both cases, molecules of different kinds move through the column at different rates, so that the sample is broken up into its components, each leaving the column at a different time.

➤ THE CLINICAL GAS PARTITIONER *requires only a tenth of the sample and a quarter of the time of the traditional Van Slyke blood gas analysis. It gives a permanent record (on the right), and its results correlate well with those of the traditional method.*

If the flow-rate of the carrier gas, dimensions of the column, and other variables are kept constant, the order in which gases emerge from the chromatographic column can be used to identify them. A suitable detector measures each component as it appears.

The Clinical Partitioner uses two chromatographic columns in series, with a detector at the exhaust of each column. The first column removes carbon dioxide from the sample mixture and holds it until oxygen and nitrogen have been separated and exhausted. The second column separates the oxygen and nitrogen.

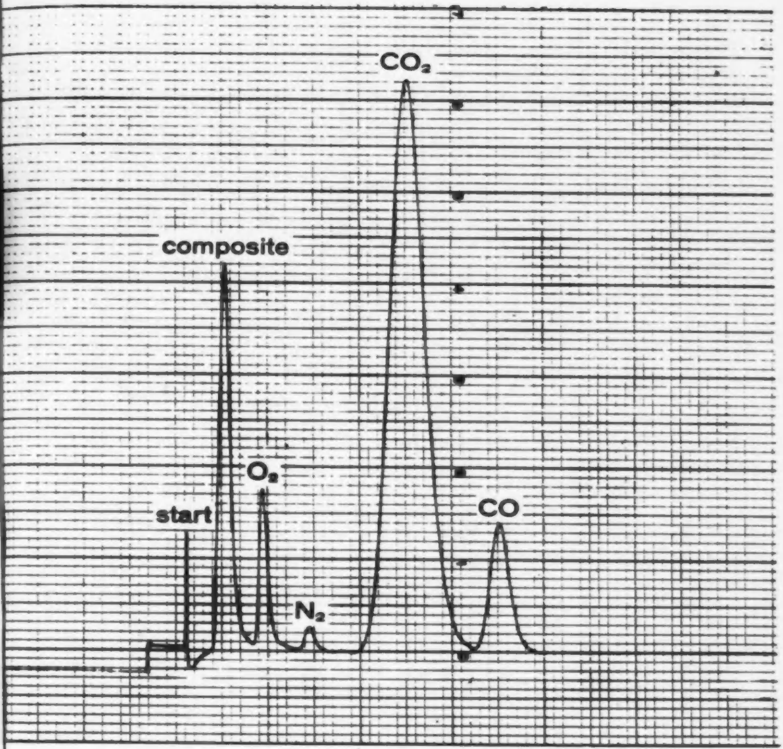
Special Reaction Chamber

Automatic determination of the gases in blood and serum is made possible by the reaction chamber.

Helium carrier gas enters the bottom of the chamber and passes through a porous Teflon disc into the upper section, into which the reaction chemicals (similar to those for Van Slyke analyses) and the blood or serum sample have been injected through a self-sealing serum cap. A magnetic stirrer agitates the mixture at a constant rate. The rising helium, dispersed by the Teflon disc, flushes the extracted gases out of the reaction mixture and carries them into the chromatographic system. The Partitioner's reaction chamber holds chemicals enough for 6 to 8 blood or serum samples.

The Fisher Clinical Gas Partitioner is compact, 18″ long, 13″ front-to-back, and 7¾″ high, with a Formica-laminated wood top and base that help insulate the instrument from local temperature changes. The instrument operates from 115-volt 50-60 cycle a-c.

Further information may be obtained by writing to Fisher Scientific Co., 334 Fisher Building, Pittsburgh 19, Pa.



➤ THE CHROMATOGRAM *shows clear proof of poisoning by carbon monoxide in the blood sample. The volume contained under each peak is proportional to the amount of the corresponding gas.*

Another In Series on Chemical Organizations

American Rocket Society

➤ THE AMERICAN ROCKET SOCIETY is the largest organization devoted solely to the advancement of the field of astronautics and related sciences. ARS now numbers over 14,000 members, a growth of more than sixfold in five years, making it one of the most rapidly growing professional engineering societies in the United States.

In accordance with the Society's purpose to promote the sciences of rocketry and space flight, it has in its 29-year history led the effort to obtain for this country a superior space program. In two instances in particular ARS programs led directly to action by the government in the space field.

In November, 1954, the ARS Space Flight Committee, headed by Milton Rosen, presented a proposal to the National Science Foundation calling for the Foundation to sponsor a study of the utility of an unmanned earth-satellite vehicle. This proposal was one of the factors which, a few months later, led to the announcement by President Eisenhower that the U. S. would launch a satellite in the course of the International Geophysical Year.

In October, 1957, ARS submitted to President Eisenhower a full-scale report calling for immediate initiation of a long-term national space flight program to be administered by a new independent government agency with broad powers in this area. The report, drawn up before the Sputnik I launching by the ARS Space Flight Committee, headed by Krafft A. Ehricke of Convair-Astronautics, and including many of this country's top astronautical engineers and scientists, led to the establishment of the National Aeronautics and Space Administration, the nation's present civilian space agency.

Publications

The Society, which is comprised of and dedicated to astronautical scientists and engineers, carries out its objectives principally through the dissemination of information in its two publications, *Astronautics* and *ARS Journal,* and through its technical meetings, numbering over 400 per year on both a local and national level.

Astronautics covers topics of broad industry interest, written to keep the specialist in one area abreast of developments in other areas that affect his specialty. It also carries general industry news including contract awards, personnel news, patents and new product announcements.

ARS Journal is a more technical publication covering in detail research and development work of particular interest to the specialist, keeping him up to date on the latest work being done in his field. Starting in the fall of 1959, ARS, under the sponsorship of the National Science Foundation, printed a quarterly supplement of translations of articles appearing in Russian technical journals on the latest results of research in the USSR in the field of astronautics which previously had been unavailable in English.

Meetings

The technical meetings fall into two categories — the large national meetings and the smaller specialist conferences. The Society holds two major meetings a year, the annual and the semi-annual meetings. At these two, all the astronautics disciplines are represented so that at one meeting, the scientist and engineer can hear not only of late developments in his particular area, but also acquaint himself with the state of the art of allied fields. The specialist conferences, on the other hand, devote themselves to a more exhaustive study of a specialized segment of astronautics drawing upon that part of the membership working in that field.

Behind the programs of these meetings and contributing to the quality of material carried by the two publications are 22 technical committees which solicit, screen and program material for presentation. These technical committees, covering specialties from astrodynamics to underwater propulsion, are headed by scientists and engineers prominent in the specialty and supported by committee members also distinguished in the field, providing the highest quality panel for selecting material most appropriate for presentation to the membership. The Society also makes seven awards annually to people who distinguished themselves in various fields of astronautics.

In addition, the membership is organized into 51 sections in their home communities, which meet on the average of once a month. These meetings give members a chance to get together on a social basis to exchange views and ideas, in addition to giving them an opportunity to participate in field trips to places of interest to their work and to hear outstanding lecturers in their fields.

Similarly, the Society has 35 student chapters formed at universities and colleges throughout the country which organize students studying in the field in groups to encourage and augment their work and to give them contact with scientists and engineers working in the field.

History

Though most recognition has been given to the Society in the post Sputnik era, it was organized on April 4, 1930, by a group of 11 men and one woman, primarily science fiction writers, for the purpose of promoting interest in space flight. Of the original dozen only one man, Dr. G. Edward Pendray, is still a member of the Society, but the organization spawned by this group has continued to grow.

The founders originally named the group the American Interplanetary Society but changed its name to the present one in 1934 because, as the editor of *Astronautics* explained at the time, "In the opinion of many members, adoption of the more conservative name, while in no way implying that we have abandoned the interplanetary idea, will attract able members repelled by the present name."

In June of 1930, the group printed its first publication, at first in mimeograph form, titled *The Bulletin,* and subsequently retitled *Astronautics,* then *The Journal of the American Rocket Society, Jet Propulsion* and now *ARS Journal*. In August, 1957, the Society began publication of its second magazine *Astronautics*.

In 1931, inspired by a trip by Dr. Pendray to Europe on which he talked with leading European scientists working with rockets, the Society formed an Experimental Committee with Dr. Pendray as chairman. This group designed the first ARS rocket, consisting of two parallel cylindrical tanks of standard aluminum piping, each 5½ feet long and 2 in. in diameter. They were held at the top by a frame piece which supported the motor and its cooling jacket, turn-on valves that could be operated electrically from a distance, and a cone-shaped nose piece containing a parachute. At the rear of the rocket were large sheet-aluminum fixed vanes for guiding in vertical flight. The fuels were gasoline and liquid oxygen.

The rocket received its first burning test on November 12, 1932 on a farm near Stockton, N. J., and though it performed as desired it was accidentally damaged in testing and therefore never flight tested.

A streamlined version of the rocket, dubbed ARS rocket No. 2, was shot in a field at Marine Park, Great Kills, Staten Island, N. Y., on May 14, 1933. It reached an altitude of about 250 feet, after firing about two seconds and was still going when a stuck valve caused the oxygen tank to explode. This firing was followed by two subsequent ones in September of 1934.

The Society then began a series of proving stand tests, which, though dogged with difficulties, resulted in the development by James Wyld of his regenerative motor which subsequently was the basis for the organization of Reaction Motors, Inc. in New Jersey.

The Society continued to grow through the early forties, but it was still too small and localized, it was felt, to organize national meetings on its own, so in November of 1945 an agreement was reached with the American Society of Mechanical Engineers under which the Society received more adequate office space and held its national meetings in connection with those of the ASME. However, as the Society grew, its meetings became too large to be merely an adjunct of another meeting and beginning with the 1958 Annual Meeting, ARS held its national meetings separately.

In August, 1955, the Society moved to 500 Fifth Avenue, from the one-room office it had occupied for several years in the Engineering Societies Building, 29 W. 39th St., New York.

Although the Society in its infant days engaged in experimentation, it became obvious after the war that rocket development was of such gigantic scope that it was beyond the abilities of a professional society. The Society holds that amateur experimentation is extremely hazardous and has taken a strong stand against any rocket experimentation outside of military or government or industry facilities. Its sections now are actively working to divert the interest, and energies devoted to amateur experimentation to activities more fruitful to the development of astronautical specialists and less harmful to eyes, arms and lives of the participants.

√ Answers to CHEMISTRY QUIZ on Page 35. √

A - 1; B - 3; C - 1; D - 1; E - 2.

New Chemical Patents

To obtain copies of these new patents, order them by number from the Commissioner of Patents, Washington 25, D. C. Enclose 25 cents in coin, money order or Patent Office Coupons (but not stamps) for each patent ordered.

Food Preserved by Radiation

➤ PROCEEDING from the assumption that storage life of foods can be increased several hundred times by inhibiting bacterial and mold growth using a combination of refrigeration and prolonged exposure to low-intensity radiation, Edgar S. Stoddard of Berwyn, Ill., has invented a food irradiating process whose patent rights he has assigned to the General Electric Company.

The process, for which he received patent No. 2,920,969, calls for subjecting food to periodic small-dosage irradiation in a combination refrigerated food storage and irradiation chamber. It aims at prolonging the storage life of foodstuffs, such as chopped meat, fresh vegetables and fruit, for a matter of several weeks.

Electrolytic Protection for Ships

➤ THE SUBMERGED metal parts of ships may be protected against corrosion by an electrolytic device.

Ernst Vossnack and Jan Hendrick Visscher, of The Netherlands, have been awarded patent No. 2,916,429 for this device whereby the ship's skin is protected by means of a D.C. current, the negative electrode of which is connected to the ship's skin, while the positive electrode is submerged and electrically insulated from the ship. Patent rights were assigned to Koninklijke Rottesdamsche Lloyd N. V. of Rotterdam.

Similar devices are already known, but suffer from two main disadvantages. The positive electrodes are fitted to the ship below the water-line, and thus the ship has to be docked for fitting and servicing, and also the field formed in the water is not sufficiently uniform.

In this case the positive electrode consists of a number of wires, or bundles of wires, of aluminum which are trailed behind the ship. Thin wires are used so that, should the wires become entangled with the screw, they will break easily and thus not damage the screw. The trivalency of aluminum ensures that the weight loss from the wire will be minimized. Such an arrangement is found to provide a uniform field around the ship.

Vaporization Cools Missiles

➤ AN EVAPORATIVE cooling system for aircraft and missiles traveling at supersonic speeds incorporates the coolant distribution within regular insulating material. Heat is removed by vaporization and by contact of the escaping and relatively cool vapor with adjacent heated areas. Inventors David W. Fox of Hyattsville and Robert M. Rivello of Silver Spring, Md., assigned rights to patent No. 2,922,291 to the U. S. Navy.

Deuterium Separated

➤ FOR SOME YEARS various methods have been used to extract heavy water, D_2O or HDO, from natural water, or else heavy hydrogen or deuterium from hydrogen. These have mostly been cumbersome and expensive, since natural sources are only about 0.015% rich in deuterium.

Patent No. 2,908,554 has been granted to Jan Hoogschagen, of The Netherlands, for his improved deuterium recovery process. He assigned patent rights to Stamicarbon N. V. of Heeoten, Netherlands.

Mr. Hoogschagen's method involves the catalytic transfer of D_2 from water to hydrogen in a counter-current system, coupled with low temperature rectifacation of the enriched hydrogen.

Vitamin B-12 Retained

➤ A DIFFICULTY in vitamin B-12 therapy is keeping the vitamin in the blood for extended periods of time. When injected into the blood stream, the vitamin rapidly reaches such a high blood concentration that it is eliminated in the urine within about 24 hours.

Robert E. Thompson of Momence, Ill., has discovered a vitamin B-12 preparation that can be retained in the blood for up to two weeks without reaching the degree of concentration that would cause it to be excreted in a patient's urine.

His preparation, for which he received patent No. 2,920,015, comprises a vitamin B-12 active substance in combination with zinc and tannic acid. Patent rights were assigned to Armour and Company, Chicago.

Method Purifies Old Auto Oil

➤ DIRTY OIL from automobile crank cases may be purified to usable oil at a commercially feasible cost by a newly patented process.

Dirty crank case oil contains many impurities, such as lint, dust, water and metal filings. Lack of an economical method of purifying this oil has resulted in most of it being discarded.

George Kostyreff of New York City has devised a process whereby this purification can be done so inexpensively "that it is now commercially practicable." He claims the resulting usable oil has properties at least equal to the properties of the original oil before it has been used.

Mr. Kostyreff's method, for which he received patent No. 2,922,758, consists essentially in dehydrating the used oil by evaporation, treating the dehydrated oil with sulfuric acid, and separating the sludge from the clear oil. The clear oil is next treated with an adsorbent with heating and steam. It is then filtered, and deodorized if necessary, to result in a pure oil that may be reused "for all purposes for which the original could be used."

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Book Condensations

Advances in Protein Chemistry—Vol. XIV — C. B. Anfinsen, Jr., and others, Eds. — *Academic,* 520 p., illus., $14. Seven reviews on such subjects as the specificity of protein biosynthesis, and sulfur chemistry of proteins.

Lipide Chemistry — Donald J. Hanahan, Frank R. N. Gurd and Irving Zabin — *Wiley,* 330 p., $10. Examines and evaluates progress made during the last ten years.

Animal-Glue Testing for Paper Sizing — P. B. Davidson and H. B. Bodenhagen — *Mellon Institute,* 14 p., illus., paper, free upon request direct to publisher, 4400 5th Ave., Pittsburgh 13, Pa.

Chemical Magic: Mystery Demonstrations for Science Clubs, Classes, and General Entertainment Programs — Leonard A. Ford — *Denison,* 141 p., illus., $3.50. Directions for more than 100 chemical tricks.

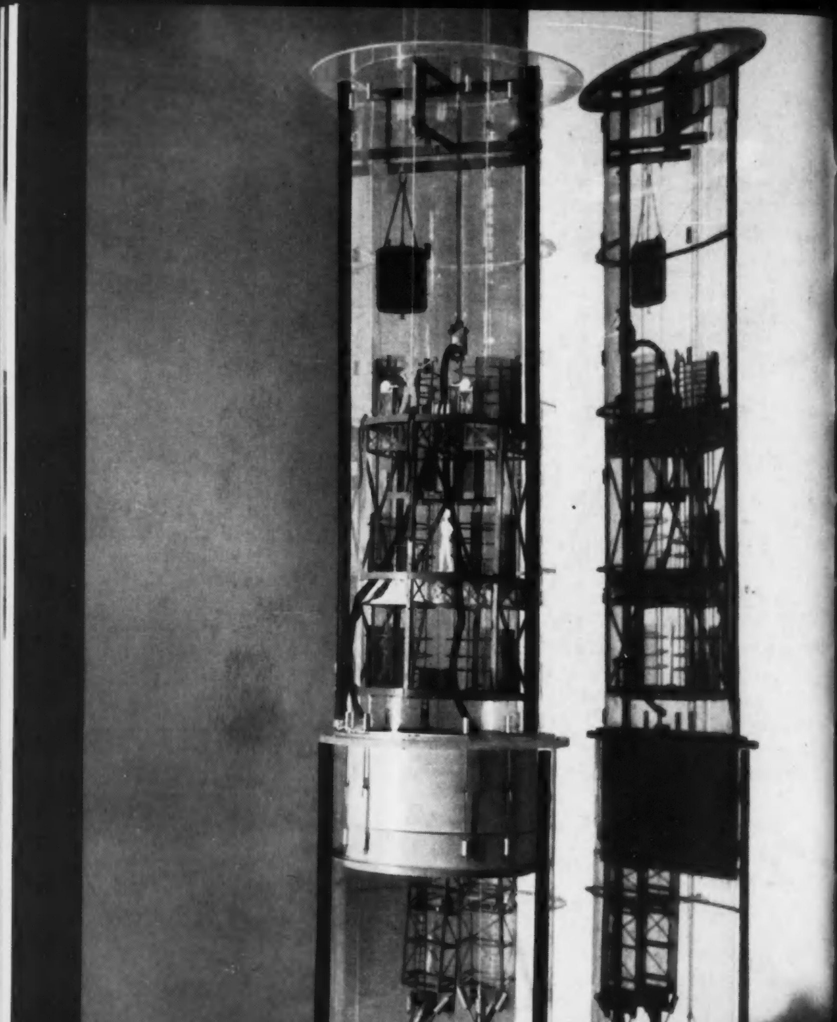
The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry — Linus Pauling — *Cornell Univ. Press,* 3rd ed., illus., $8.85. Revision includes treatment of the electronic structure of atoms, atomic energy levels, electron spin, the Pauli exclusion principle, and the magnetic moments of atoms.

Valency: Classical and Modern — W. G. Palmer — *Cambridge Univ. Press,* 2nd ed., 244 p., $5.50. Deals both with the old-established concepts of chemical valency and with the modern electronic theories.

The Foundations of Chemical Kinetics — Sidney W. Benson — *McGraw,* 703 p., $13.50. Broad survey of the field of kinetics at senior and graduate level, emphasizing the kinetics of gas reactions.

On the Back Cover

➤ Our Back Cover *shows, in model form, an ingenious time-saver for deep mine shaft sinking which is being built for use by the Canadian subsidiary of International Minerals & Chemical Corporation to complete a 3,000-foot shaft at its potash mine project in Saskatchewan, Canada. The mobile "triple-decker" arrangement allows simultaneous activity at three levels in the main phases of shaft sinking, mucking or digging, preparation of concrete forms, and the pouring and finishing of the concrete shaft lining, and can make sinking three times faster. The entire unit, including the mechanical diggers, moves up and down the shaft. This is the first use of this triple-decker principle in the Western Hemisphere. Similar operations have been employed with great success in deep-shaft sinking for South African mines. The IMC mine, near Esterhazy in eastern Saskatchewan, will produce from the world's greatest known reserve of high grade potash ore.*



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